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Evaluation of Durability of Portland-Cement-Based Grout for Subsurface Applications at OU 7-13/14

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Idaho Cleanup Project

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ABSTRACT

This report evaluates the durability of cementitious grouts when used for in situ grouting of transuranic and low-level mixed waste, typical of waste buried in the Subsurface Disposal Area, a radioactive landfill at the Radioactive Waste Management Complex, part of the Idaho National Laboratory Site. Application of in situ grouting at the Subsurface Disposal Area can accomplish three possible purposes: reducing migration of contaminants, supporting cap and overlying material, or simplifying retrieval (by improving safety and reducing dust). Durability is important to immobilization of contaminants and support of a cap, but is not important to retrieval since the grout would not remain in situ for a long time. Cementitious grouts can reduce migration of contaminants both by coating waste material and by restricting the access of water to contaminants and waste. Cementitious grouts also can provide structural support by eliminating voids and forming contiguous columns to prevent subsidence.

Durability of Portland-cement-based grouts was evaluated using an extensive literature search, previous tests of in situ grouting at the Idaho National Laboratory Site, and information available from tests currently being conducted at the Idaho National Laboratory Site. This evaluation includes developing a review of behavior using standard test procedures applicable to grouts (e.g., contaminant leaching and compressive strength), as well as behavior under possible harsh conditions at the Subsurface Disposal Area that could affect the long-term stability of Portland-cement-based grouts. Results will be used to support the feasibility study for Waste Area Group 7, Operable Unit 7-13/14.

EXECUTIVE SUMMARY

The purpose of this report is to evaluate the durability of Portland-cement-based grouts when used for in situ grouting of transuranic and low-level mixed waste, typical of what is buried in the Subsurface Disposal Area (SDA), a radioactive landfill at the Radioactive Waste Management Complex, part of the Idaho National Laboratory Site. Application of in situ grouting at the SDA can accomplish three purposes: reducing migration of contaminants, supporting cap and overlying material, or simplifying retrieval of waste. Durability is important to reducing migration of contaminants and supporting an eventual barrier cap, but is not important to retrieval since the grout would not remain in situ for a long time. Portland-cement-based grouts can immobilize contaminants by coating buried waste and by restricting the access of water to contaminants and waste. Portland-cement-based grouts also can provide structural support by eliminating voids and forming contiguous columns to prevent subsidence.

Portland-cement-based grouts have the following desirable characteristics for use at Idaho National Laboratory Site:

- Low permeability to water, which reduces the likelihood of contaminant transport

- Substantial penetration into possible voids in the soil-waste matrix, improving long-term stabilization of waste

- Reduction of the generation of dust and particulates that could spread contamination should waste retrieval eventually be desired.

Information on Portland-cement-based grouts was identified using an extensive literature search, previous tests of in situ grouting at the Idaho National Laboratory Site, and information available from tests currently being conducted at the Idaho National Laboratory Site. These results were reviewed, and an evaluation of the expected performance of these cementitious grouts was made based on current and projected grouting plans for the SDA. This evaluation includes a review of behavior developed using standard test procedures applicable to grouts (e.g., contaminant leaching and compressive strength), as well as the behavior for possible harsh SDA conditions that could affect the long-term stability of Portland-cement-based grout, including biodegradation and radiolysis. Results will be used to support the feasibility study for Waste Area Group 7, Operable Unit 7-13/14.

Results from the literature search include grouts with relatively standard Portland cement compositions and grouts that have proprietary compositions. Proprietary grouts that are included in this report are GMENT-12, TECT, TECT HG, U.S. Grout, and Saltstone[a]. The following conclusions are based on the findings of the literature search and results assessment for these cementitious grouts:

- Short-term reactions of Portland cement are primarily related to the hydration, or cure, of the freshly cast grout. The hydration mechanisms of cement pastes are a complex series of chemical reactions, dissolutions, precipitations, exchanges, and crystallizations, which can be disturbed in many different ways.

- Many chemical species have been demonstrated to have an effect on the cure reactions of grout. Many common anions and cations can be accelerators or retarders of Portland cement. The

a. References herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government, any agency thereof, or any company affiliated with the Idaho National Laboratory.

effectiveness of acceleration by specific cations is given in order of decreasing effectiveness as follows: $Ca^{2+} > Ni^{2+} > Ba^{2+} > Mg^{2+} > Fe^{3+} > Cr^{3+} > Cu^{2+} > La^{3+} > NH^{4+} > K^{+} > Li^{+} > Cs^{+} > Na^{+}$. The effectiveness of retardation by specific cations is given in order of decreasing effectiveness as follows: $Cu^{2+} > Zn^{2+} > Pb^{2+}$. The effectiveness of acceleration by specific anions is given in order of decreasing effectiveness as follows: $OH^{-} > Cl^{-} > Br^{-} > NO_3^{-} > SO_4^{2-} > CH_3CO_2$.

- Calcium chloride is the most widely used cement accelerator. Most inorganic electrolytes, especially soluble calcium salts, accelerate the hydration reaction. Many chemical species (organic and inorganic compounds) can retard the set of grout.

- Relatively constant moderate temperatures and relatively constant soil-water content in the SDA preclude physical damage to Portland-cement-based grouts from freeze-thaw cycles and from shrinkage and swelling caused by changes in the moisture of surrounding material resulting from wet-dry cycles.

- The four major metals of interest with respect to corrosion in the SDA are carbon steel, stainless steel, inconel, and beryllium. Corrosion of metal is a concern in two ways. First, the products of corrosion from metal take up more volume than the original metal, leading to localized regions of stress within cement near the encased metal. Second, the metal may contain contaminants. As the metal corrodes, the contaminants can be released from the metal. Both mechanisms are of interest in the SDA.

- Because of the use of steel in commercial construction, a lot of information about corrosion of carbon steel, especially rebar, in concrete is available in the literature. Studies of stainless steel also are available because it is used for reinforcing some commercial construction. Inconel and beryllium are not used for reinforcing, and no data could be located on their behavior in concrete. However, it is known that beryllium is vigorously attacked by aqueous alkaline solutions and, before setting, Portland cement is essentially an aqueous alkaline solution with a pH of 12 (Miller and Boyd 1967).

- Chloride is a major agent of attack of carbon steel within concrete, although it is not expected to be a major factor at the SDA. Carbonation and groundwater leaching of cement in the grouted waste is expected to occur and could reduce the alkalinity (lower the pH) of the cement, leading to a more corrosion-favorable environment for metals.

- Results from leach tests on Portland-cement-based grouts for the basic constituents of Portland cement (i.e., calcium, silicon, and aluminum) show very low rates of leaching. Using these results to calculate the timeframe when 1% of these constituents will be leached from a grout monolith indicated that "tens of thousands of years" would be required (Loomis et al. 2002).

- Accurately assessing the effect of the dose received by the grouts is difficult because of a lack of isotopic content information for some radioactive packages buried in the SDA. A conservative approach indicates that radioactive doses are sufficiently high to result in a reduction of compressive strength ranging from 15 to 60%. Reductions in compressive strength within this range would not cause most grout-waste mixtures to drop below the minimum 60 psi required by the Nuclear Regulatory Commission technical position on waste form to provide adequate support to the overlying material.

- Degradation of cement-based grouts can result from in situ attack by microorganisms (i.e., microbial-induced corrosion). Microbial-induced corrosion of concrete is a function of the macroenvironmental conditions, the changing microenvironmental conditions, and the bioavailability of nutrients and energy.

- Microbial-caused concrete degradation rates in concrete sewer structures are as high as 4.3 to 4.7 cm/yr (1.69 to 1.85 in./yr). Sewer systems offer high sulfur and nutrient concentrations, and well mixed and oxygenated aqueous conditions. Biocorrosion rates elsewhere are generally slower, ranging from 1 to 5 mm/yr (0.04 to 0.2 in./yr), but studies have reported rates as high as 1 cm/yr (0.4 in./yr). Compared to the expected composition of the groundwater in the SDA at the Idaho National Laboratory Site, the solutions used in the reported studies contain more nitrogen (ammonia), phosphorous, and potassium than groundwater and have a much lower pH, favoring acid-producing bacteria. In addition, studies were conducted at higher temperatures (25°C [77°F]) than would be expected in the subsurface (7 to 10°C [44.6 to 50°F]), and the SDA provides unsaturated rather than saturated conditions. In situ degradation at the SDA likely would occur, but at rates slower than those reported in the literature.

- Carbonation of cement can alter the performance of the cement by reducing the pH, changing the mineralogy, and altering the physical properties of the cement. Carbonation occurs when carbon dioxide (gas phase) or bicarbonate (liquid phase) diffuses into cement and reacts with the existing mineralogy. While carbonation is generally a slow process, the rate depends on the concentration of carbon dioxide (or bicarbonate) and the degree of hydration of the cement. The estimate of the carbonation rate for the SDA was interpolated from carbonation rates given in the two models based on the carbon dioxide concentration in the soil in the SDA compared to concentrations of carbon dioxide used in the models. In 1,000 years, the carbonation front in the SDA is estimated to move 73.4 mm (2.89 in.) into the cemented waste.

- Groundwater leaching can degrade performance of cement over time. The Nuclear Regulatory Commission has developed a model to predict migration from groundwater leaching of a 10.5 pH front into concrete. The conditions for in situ grouting at the SDA are expected to be very similar to those used for the model. The model predicts that the 10.5 pH front will move toward the center of the concrete mass at a rate of 1 m (3.3 ft) per 1.5×10^5 years or 6.67×10^{-3} mm per year.

- Results from recent testing show that compressive strength values for the Portland-cement-based grouts and grout-waste mixtures typical of those expected in the SDA are significantly above the minimum (i.e., 60 psi) required by the Nuclear Regulatory Commission technical position. Whether these compressive strengths will be adequate to support an overlying cap will need to be determined based on the specifics of the cap design and the grout placement strategy.

- Hydraulic conductivity values for grout and grout-waste mixtures were in the range of 10^{-6} to 10^{-8} cm/sec, which is about two orders of magnitude less than the average hydraulic conductivity of the SDA soil. This difference demonstrates the relative impermeability of grouted waste when compared to soil.

- Porosity testing for three proprietary grouts mixed with soil showed two of the grouts reduced the mixture porosity by small amounts. Porosity for these mixtures does not appear to be closely coupled with hydraulic conductivity.

- It was expected that the leach index would decrease as the waste loading increased for tests conducted with sludge that includes radionuclides. This was not observed as the concentrations of radionuclides in the leachate were below the detection limit, so that the leach index was calculated from the detection limit. Most of the leach indices are greater than 10, indicating a low effective diffusivity and a high resistance to leaching.

- The effective diffusivity of the transuranic radionuclides in the cementitious grouts was lower than the effective diffusivity of Tc-99, C-14, and I-129 in the cementitious grouts. Cementitious grouts immobilize contaminants by a combination of chemical interaction and encapsulation. The difference seen between the two classes of radionuclides with the cementitious grouts is likely from a difference in the chemical interactions between radionuclides and grouts.

- Leach tests, similar to those performed with proprietary grouts and nontransuranic radionuclides, were conducted for nonproprietary grouts (i.e., Portland cement, Portland cement with fly ash, Portland cement with slag, Portland cement with fly ash and sodium thiosulfate, and Portland cement with slag and sodium thiosulfate). Leach results showed there are no statistically significant differences between these Portland-cement-based grouts. Comparison of nonproprietary and proprietary results shows that care should be taken in grout selection, as some grouts perform better than others.

- Accelerated leach tests show that TECT grout is effective in preventing leaching of chromium and lead. Toxicity characteristic leaching procedure leach tests indicate that none of the cementitious grouts alone are effective in preventing mercury leaching. Adding a material with a high affinity for mercury to the grouts (about 2 wt% of sodium sulfide) reduced mercury leaching to below current limits for all cementitious grouts tested.

CONTENTS

FIGURES

TABLES

ACRONYMS

ASTM	American Society for Testing and Materials (now ASTM International)
INL	Idaho National Laboratory
ISTD	in situ thermal desorption
MIC	microbial-induced corrosion
NRC	Nuclear Regulatory Commission
OU	operable unit
RI/FS	remedial investigation and feasibility study
RWMC	Radioactive Waste Management Complex
SDA	Subsurface Disposal Area
TCLP	toxicity characteristic leaching procedure
TRU	transuranic
WAG	waste area group

Evaluation of Durability of Portland-Cement-Based Grout for Subsurface Applications at OU 7-13/14

1. INTRODUCTION

This report presents an evaluation of currently available data about the physical and chemical characteristics of Portland-cement-based grouting material to understand better its expected performance when injected in situ in buried radioactive waste. This in situ injection is expected to increase the long-term stability of waste buried in the Subsurface Disposal Area (SDA), a radioactive landfill that is part of the Radioactive Waste Management Complex (RWMC) at the Idaho National Laboratory (INL) Site. In situ injection of cementitious grouts can be used to create contiguous columns that reduce infiltration of moisture into soil and waste and to provide additional support to reduce the potential for subsidence of overlying material.

In situ jet grouting has been identified as a method of stabilizing waste in the SDA (Holdren and Broomfield 2003). Tests of jet grouting carried out at the INL Site have indicated that Portland-cement-based grouts have several qualities that are necessary for jet grouting in the SDA; however, additional information is needed about the performance, durability, and long-term behavior of cementitious grouts under conditions at the SDA to ensure they perform as required.

This report combines information from tests of in situ jet grouting at the INL Site over a previous nine-year period, available information from tests now being carried out, and results from an extensive literature search to evaluate the performance of Portland-cement-based grouts under specific conditions in the SDA.

1.1 Purpose

The purpose of this report is to evaluate the durability of Portland-cement-based grouts when used to grout transuranic (TRU) and low-level mixed waste, typical of that in the SDA. This report presents an evaluation of information from a broad range of literature to better understand the expected performance of cementitious grouts at the SDA. Results from this work will support risk assessment, preremedial design studies, and a better understanding of expected grout behavior for the feasibility study (FS) for Waste Area Group (WAG) 7, Operable Unit (OU) 7-13/14.[b] The plan describing the requirements for the remedial investigation and feasibility study (RI/FS) is in the *Second Revision to the Scope of Work for the OU 7-13/14 Waste Group 7 Comprehensive Remedial Investigation Feasibility Study* (Holdren and Broomfield 2003).

1.2 Overview

Field-monitoring data and modeling of contaminant fate and transport suggest that release and migration of mobile, long-lived fission and activation products pose the most immediate health risk from the SDA (Holdren et al. 2002). Grouting is one of several potential remedial alternatives for the SDA; grout materials based on Portland cement are being considered.

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b. The Federal Facility Agreement and Consent Order lists 10 WAGs for INL. Each WAG is subdivided into OUs. The RWMC is identified as WAG 7 and originally contained 14 OUs. Operable Unit 7-13 (TRU pits and trenches RI/FS) and OU 7-14 (WAG 7 comprehensive RI/FS) were ultimately combined into the OU 7-13/14 comprehensive RI/FS for WAG 7.

Grouting at the SDA can be used to produce one or more of these three potential applications: immobilizing contaminants, supporting a cap and overlying material, or simplifying waste retrieval. Durability is important to immobilizing contaminants and supporting a cap but is not an issue for simplifying retrieval since the material does not remain in situ for a long time.

Grouting can immobilize contaminants through microencapsulation, macroencapsulation, chemical binding, exclusion of water, or a combination of the four; these mechanisms are not independent, but each emphasizes a different portion of the complex set of mechanisms involved in immobilization of contaminants. Portland-cement-based grouts can be effective for all four of these immobilization processes, depending on the waste composition and form. Cementitious grouts coat many typical waste materials, including paper and soil. When waste materials are finely divided and easily wetted by cement paste or when larger particulates (i.e., chunks of soil or sludge) mix with the injected cement-based grout, the waste is microencapsulated. Chemical binding of some waste materials with cementitious grouts may take place, depending on the composition of the waste. Additives can selectively enhance chemical binding (e.g., addition of sodium sulfide to enhance binding of mercury). Cementitious grouts also immobilize contaminants by restricting water contact with the contaminants. Portland-cement-based grouts generally have low porosity and low hydraulic conductivity, properties that work together to exclude water from grout-coated materials. The long-term durability of Portland-cement-based grouts is very important to their performance as materials for immobilization of contaminants, since many of the contaminants of concern in the SDA have long half-lives.

Preventing subsidence of an overlying cap is important to ensure that water will not infiltrate into buried waste. Two different grouting approaches may be used in preventing subsidence. In the first approach, grouting relatively large areas of the SDA eliminates voids within the waste, which prevents future subsidence and cap damage. Grouting to eliminate voids results in a series of contiguous columns being formed within the SDA. The purpose of the contiguous columns is to prevent subsidence; they are not the primary support for the cap. Therefore, the strength of the contiguous columns of grout only must be sufficient to support the soil and cap directly above the grouted region. Durability of the contiguous grout columns for this purpose is important primarily in terms of immobilization. Portland-cement-based grouts can fill voids and form relatively high-strength columns.

For the second approach, local grouting at selected locations also can establish pillars that provide structural support for the cap, independent of the waste. Grouting to provide structural support columns places stricter requirements on the physical properties and durability of the grout. The compressive strength of the grout column must be sufficient to support the local regions of the overlying material and cap. The design may require that no credit is taken for support from the surrounding waste. Structural properties of the grout must be specified so that even after placement in different types of waste, the properties are sufficient to support the cap. Long-term durability of grouts used for pillars is very important, since most of the waste is not treated with grout and may not have sufficient strength to support the cap. Jet-grouted Portland-cement-based materials have relatively high strength and can be used as support pillars.

Durability is not an issue for grouting waste that will be retrieved. Cementitious grouts were shown to reduce the spread of dust and contamination during retrieval of waste (Loomis et al. 2002); however, retrieval was difficult because the cement-based monolith resembled reinforced concrete and was not easy to disassemble.

Waste composition can have a significant influence on the performance of cementitious grouts. Contaminants in the SDA include hazardous chemicals (both organic and inorganic), remote-handled fission and activation products, and TRU radionuclides. The waste is buried in pits, trenches, and soil vaults. Waste placed in the SDA is in diverse forms, including metal drums, wood and cardboard boxes, soft-side boxes, bags, and large objects. Some of the waste was stacked, and some was dumped at random. Similar surrogate test materials were jet grouted in a cold (i.e., nonradioactive) test pit (Loomis, Zdinak, and Bishop 1996). Examination of this surrogate waste revealed that while Portland-cement-based grouts did not saturate tightly bound paper products, they did fill all interstitial voids in the waste containers, which encapsulated these difficult-to-penetrate materials (Loomis et al. 2002). Testing of in situ jet grouting at the INL Site (Loomis, Zdinak, and Jessmore 1998; Loomis et al. 2002) has demonstrated the following desirable characteristics of cementitious grouts for use at the SDA:

- High compressive strength to provide support and reduce the potential for subsidence of overlying material
- Complete encapsulation of materials that cement-based grouts have difficulty penetrating
- Low water permeability, reducing the likelihood of contaminant transport.

This report documents the long-term durability aspects of Portland-cement-based grouts with respect to structurally supporting an overlying cap and immobilizing contaminants within the waste.

1.3 Scope

This report summarizes a broad range of information about Portland-cement-based grouts derived from (1) testing sponsored by the INL Site (both in the past and continuing today), and (2) information from an extensive literature search to aid in understanding expected cementitious grout performance for the areas that will influence usefulness or durability. The major criteria addressed in this evaluation are the physical properties, physical stability, hydraulic conductivity, chemical stability, biodegradability, and radiation susceptibility of the grout. An assessment is included of the behavior of Portland-cement-based grouts for standard test procedures applicable to grouts (e.g., leaching), as well as expected behavior under harsh environmental conditions at the SDA that could affect long-term stability of this grout material. Results are presented for Type I and Type H Portland cements and for proprietary Portland-cement-based commercial grouts, including TECT HG, TECT, GMENT-12, U. S. Grout, and Saltstone.

1.4 Brief History and Description of the Idaho National Laboratory Site

The INL Site, originally established in 1949 as the National Reactor Testing Station, is a U.S. Department of Energy-managed facility that has historically been devoted to energy research and related activities. The INL Site is located in southeastern Idaho and occupies 2,305 km^2 (890 mi^2) in the northeastern region of the Snake River Plain. Regionally, the INL Site is nearest to the cities of Idaho Falls and Pocatello and to U.S. Interstate Highways I-15 and I-86. The INL Site extends nearly 63 km (39 mi) from north to south, is about 58 km (36 mi) wide in its broadest southern portion, and occupies parts of five Southeast Idaho counties. Public highways (i.e., U.S. 20 and 26 and Idaho 22, 28, and 33) within the INL Site boundary and the Experimental Breeder Reactor I, which is a national historic landmark, are accessible without restriction (Zitnik et al. 2002). See Figure 1 for the location of the INL Site and the major facilities.

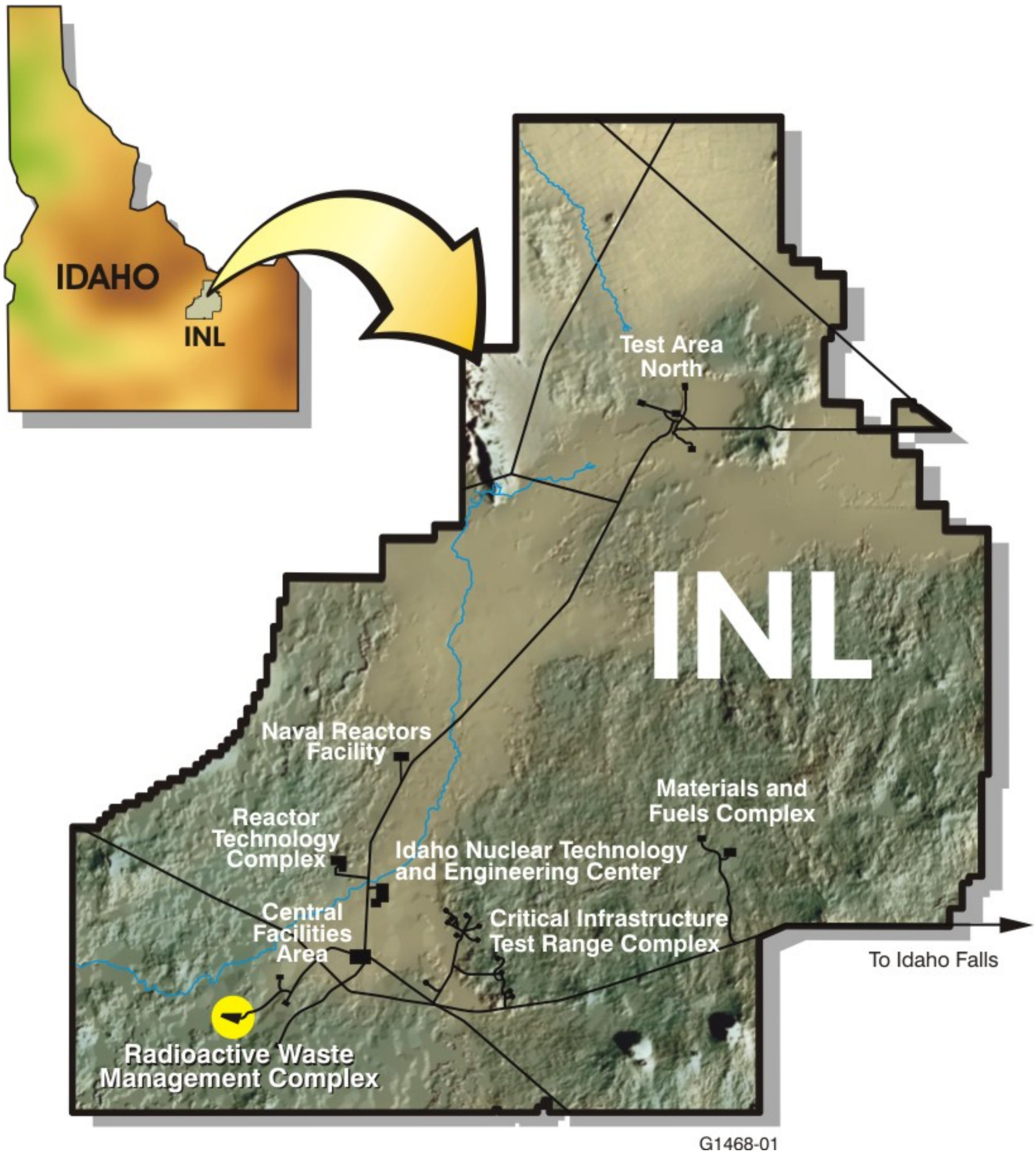

Figure 1. Map of the Idaho National Laboratory Site showing the location of the Radioactive Waste Management Complex and other major facilities.

The RWMC, located in the southwestern quadrant of the INL Site, encompasses a total of 72 ha (177 acres) and is divided into three separate areas by function: the SDA, the Transuranic Storage Area, and the Administration and Operations Area. The original landfill, established in 1952, covered 5.2 ha (13 acres) and was used for shallow land disposal of solid radioactive waste. In 1958, the landfill was expanded to 35.6 ha (88 acres). Relocating the security fence in 1988 to outside the dike surrounding the landfill established the current size of the SDA as 39 ha (97 acres). The Transuranic Storage Area was added to RWMC in 1970. Located next to the east side of the SDA, the Transuranic Storage Area encompasses 23 ha (58 acres) and is used to store, prepare, and ship retrievable TRU waste to the Waste Isolation Pilot Plant. The 9-ha (22-acre) Administration and Operations Area at RWMC includes administrative offices, maintenance buildings, equipment storage, and miscellaneous support facilities (Zitnik et al. 2002). See Figure 2 for a map of RWMC showing the location of the SDA.

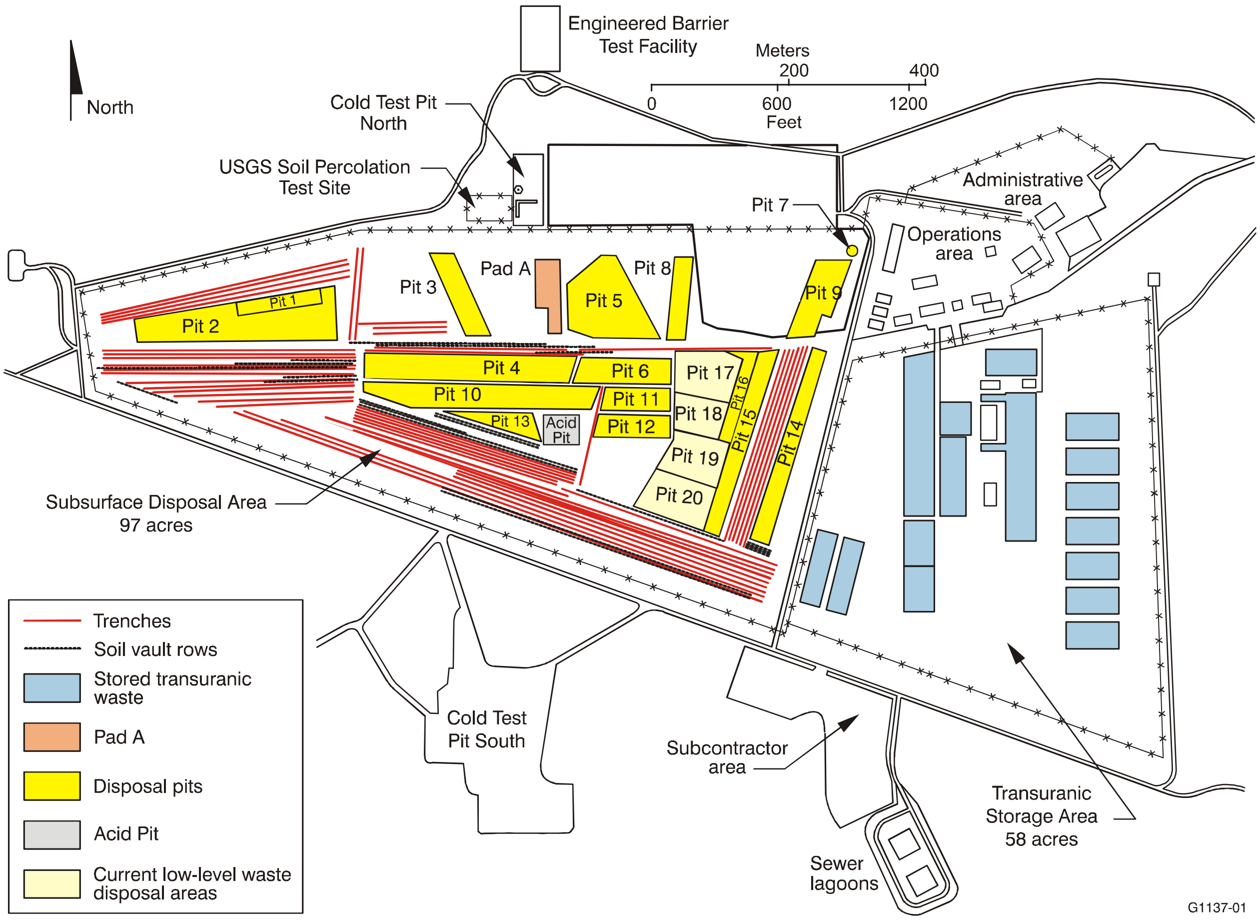

Figure 2. Diagram showing the Radioactive Waste Management Complex.

Underlying RWMC at an approximate depth of 177 m (580 ft), the crescent-shaped Snake River Plain Aquifer flows generally from the northeast to the southwest. The aquifer is bounded on the north and south by the edge of the Snake River Plain, on the west by surface discharge into the Snake River near Twin Falls, Idaho, and on the northeast by the Yellowstone Basin. The aquifer consists of a series of water-saturated basalt layers and sediment.

The surface of the SDA is a semiarid, sagebrush desert. The undisturbed surficial sediments at RWMC range in thickness from 0.6 to 7.0 m (2 to 23 ft). The subsurface below these shallow surficial sediments is characterized by alternating layers of fractured basalt and sedimentary interbeds. The regional subsurface consists mostly of these layered basalt flows with a few comparatively thin layers of sedimentary deposits, called interbeds. The interbeds tend to retard infiltration to the aquifer and are important features in assessing the fate and transport of contaminants; however, there will be little remaining stratigraphic layering in the soil used to bury waste containers. Infiltration of water occurs episodically from rain, flood, and snowmelt (Zitnik et al. 2002).

These geophysical and meteorological conditions at the SDA are important background in understanding the tests that Portland-cement-based grouts have undergone and continue to undergo and the results of those tests.

1.5 Brief Summary of Past Field Demonstrations

Testing at the INL Site over a nine-year period developed jet grouting equipment and techniques and provided important information on its effectiveness as an option for long-term stabilization of fission and activation products in the SDA (Loomis et al. 2002). The jet grouting process begins by driving a drill stem, with nozzles mounted near the bottom, to the full depth to be treated (at the SDA this is approximately 6.1 m [20 ft]). The drill stem is then rotated as grout is injected at 400 bar (6,000 psi) through the nozzles. The drill stem is withdrawn in predetermined increments, forming a column of grout-soil mixture. Depending on the expected void volume of the region to be grouted, the time interval for each step of the drill stem extraction can be adjusted (longer steps equal more grout placed). The high pressure of the grout aids in mixing the grout and subsurface material. The grouted columns are approximately 61 cm (24 in.) in diameter. A set of contiguous columns is formed by jet grouting a series of holes on a triangular pitch with a spacing of approximately 51 cm (20 in.). When the columns solidify, they form a monolith that substantially reduces the likelihood of contaminant migration.

Portland cement Type I, Portland cement Type H, TECT, and TECT HG have been successfully tested during grout-related studies at the INL Site. Following is a brief summary of the results:

- Portland Type I cement was field-tested in a pit with simulated waste; jet grouting was judged to be successful (Loomis and Thompson 1995; Loomis, Thompson, and Heiser 1995). The jet-grouted contiguous columns were destructively examined, and the grout-soil mixture was found to be heterogeneous with areas of neat grout, grout well-mixed with soil, and small inclusions of ungrouted soil. The grouted volume was free of voids. The Type I cement did not saturate the tightly bound paper products, but filled all interstitial voids in the waste containers, which encapsulated these materials that are difficult to penetrate. For simulated organic sludge (i.e., canola oil and kitty litter), the sludge and Type I cement did not mix well, and the mixture was not set and would flow. The Portland Type I cement resulted in greater reduction in dust spread compared to other dust suppression methods.

- Portland Type H cement was found to form a cohesive volume following jet grouting, except in regions where there were high concentrations of salt (i.e., sodium sulfate, a nitrate salt simulator) (Loomis et al. 2002). Destructive examination of the contiguous columns showed that the grout had not cured in the vicinity of a sodium sulfate drum. Even though the columns were porous in this region, there were no visible voids, and the waste was stabilized against subsidence. Jet grouting of Type H cement in the field-scale permeameter appeared to be successful, although the measured hydraulic conductivity was higher than expected. Shrinkage of the grout matrix from the permeameter wall was believed to have caused higher-than-expected values for hydraulic conductivity.

- Jet grouting of TECT into a pit with simulated waste (Loomis and Thompson 1995; Loomis, Zdinak, Bishop 1997) resulted in a cohesive monolith with essentially no voids. Destructive examination showed a solid set of contiguous columns with small inclusions of ungrouted soil completely surrounded by grout (see Figure 3). These inclusions represented about 15% of the columns by volume, but the region was free of voids. TECT successfully encapsulated simulated organic sludge (i.e., canola oil and kitty litter), as shown in Figures 4 and 5. TECT behaved similarly to Portland Type I cement in that it did not saturate tightly bound paper products, but filled all interstitial voids in the waste containers, which encapsulated these materials that are difficult to penetrate. TECT also filled all interstitial voids in containers of wood as shown in Figure 6.

- TECT HG was successfully used in jet grouting (Loomis et al. 1999) in the INL Site Acid Pit. Actual waste contained mercury and minor amounts of fission products in soil only.

Figure 3. Photograph of inclusions of clay soil in the TECT monolith.

Figure 4. Photograph of drum containing oil sludge encapsulated in TECT.

Figure 5. Photograph of detail showing encapsulation of organic sludge simulant kitty litter.

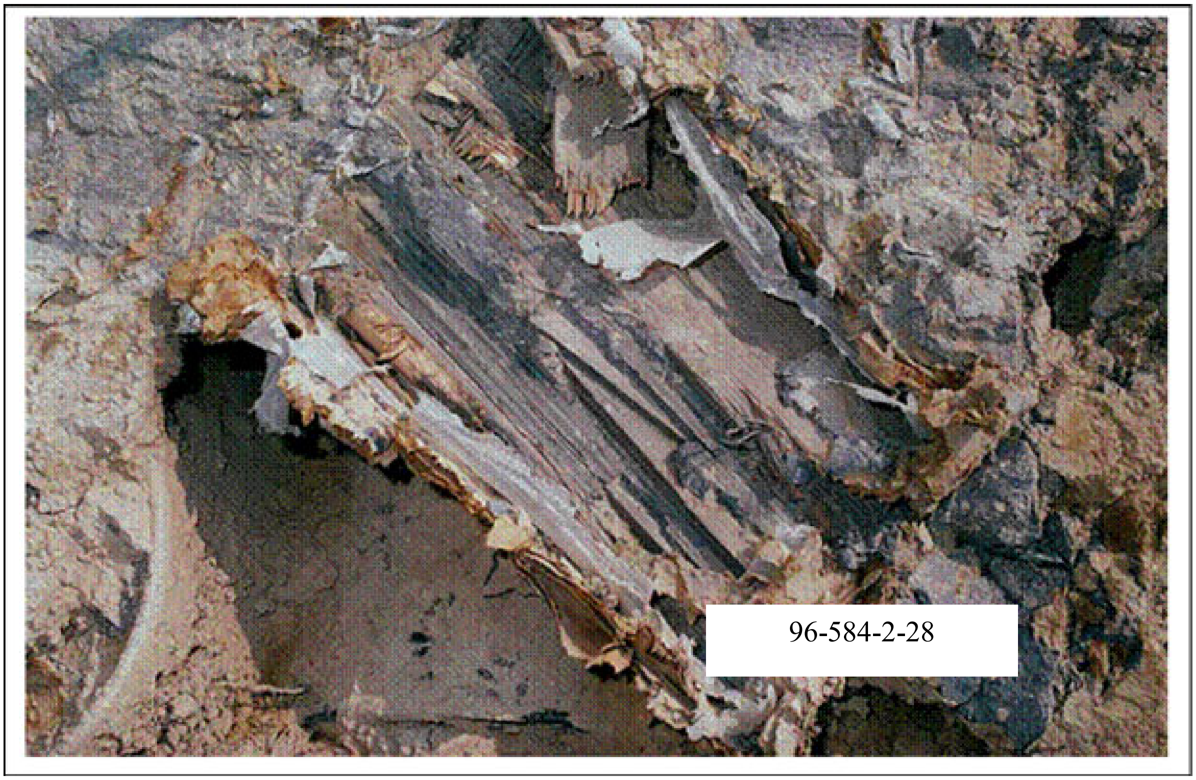

Figure 6. Photograph of drum of wood encapsulated by TECT.

1.6 Document Organization

The authors searched the literature extensively to obtain information on Portland-cement-based grouts. This information was evaluated for the expected performance of cementitious grouts based on current and projected conditions at the SDA. Initial studies were identified that included experimental work to provide needed performance characteristics for several grouts, including TECT HG and TECT (Milian et al. 1997; Heiser and Fuhrmann 1997). Results from these studies are compared with more recent results to aid in evaluating possible performance. Since much of the information obtained from the literature search is very detailed, these details have been summarized to provide a concise description of the applicability of the results in expected use at the SDA.

The following briefly describes the remaining sections in this report:

- Section 2 describes the requirements for grout used at the INL Site, including the findings of previous tests at the INL Site, and lists the characteristics for evaluating Portland-cement-based grouts.
- Section 3 summarizes information for Portland-cement types shown to be suitable for use as grouts and for proprietary, commercially-available Portland-cement-based grouts.
- Section 4 provides detailed information describing Portland-cement-based grout performance and relates this performance to the expected conditions in the SDA.
- Section 5 summarizes the conclusions developed for the durability of Portland-cement-based grout for conditions expected in the SDA.
- Section 6 contains the references cited throughout this report.

2. PORTLAND-CEMENT-BASED GROUT PERFORMANCE CHARACTERISTICS

If grouts are used in the SDA, they will be required to provide one or both of the following functions: (1) long-term support for a cap overlying the waste to prevent subsidence, and (2) long-term immobilization of contaminants. The grouts must effectively provide these functions for a very long time (i.e., many hundreds of years). In this context, a grout will be considered to be durable if it adequately performs its design functions over the desired period. Either deterioration or damage could cause a grout to fail to meet design goals. Grout deterioration can occur as a result of chemical interactions, such as exposure to small amounts of nitrate salts, or physical interactions (such as exposure to high-radiation fields over long periods). Grout damage may result from a broad range of causes, including expansion (e.g., reactions with chemicals in the environment, physical interactions such as freezing, or gas generation resulting from radiolysis), shrinkage (e.g., excess drying or interactions with chemicals), or leaching of key cement constituents.

Durability of grout has been shown to depend on the grout's chemical stability, physical characteristics, and ability to withstand harsh chemical, physical, biological, and radiation insults without unacceptable deterioration. Providing support for a cap requires adequate mechanical properties, such as compressive strength, and a grout structure that maintains these properties at acceptable levels over time. In addition, the stability of primary grout chemical constituents during leaching is a good indicator that the grout will maintain its strength in the long term.

Immobilizing contaminants may result from encapsulation of the waste to prevent water from contacting the waste and transporting contaminants, or from chemical binding of the waste within the grout. Indicators of encapsulation potential include hydraulic conductivity, porosity, and the likelihood of fracture formation. The leachability index is an indicator of the effectiveness of a grout to encapsulate and chemically immobilize contaminants.

Thus, the general characteristics of Portland-cement-based grout that will affect its long-term performance and eventual durability include its chemistry, physical and other interactions, structural support properties, and contaminant migration indicators. The following paragraphs briefly discuss each of these characteristics.

2.1 Physical and Other Interactions of Portland Cement

The long-term performance of Portland cements may degrade as a result of changes in basic cement chemistry from aging, or changes in cement chemistry resulting from interactions with chemicals in the environment. Basic Portland cement chemistry is very complex at any point in time and is metastable. This complexity, combined with a lack of performance data beyond about 150 years[c], results in potentially large uncertainties in the prediction of long-term behavior. Interactions with other chemicals are likewise complex and will be important in understanding grout performance because there are a variety of organic and inorganic chemicals buried in the SDA.

Physical and biological interactions will occur in the SDA that may influence the chemistry and physical behavior of the grouts. Examples of interactions that could reduce grout durability include:

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c. This document focuses on commercially-available Portland cement formulations for which there are approximately 150 years of industrial experience. In some cases, lime cements, such as those used in antiquity, have shown stability for 2,200 years (EDF-2490, EDF-5333). As will be discussed in the sections that follow, a key issue for the long-term stability of any type of cement is whether the cement remains at equilibrium with its surroundings without substantial weathering or leaching of constituents.

- Freeze-thaw cycles—Repeated freezing and thawing over a prolonged period reduce the performance (e.g., crack formation and surface spalling) of cement-based grout.

- Wet-dry cycles—Repeated water saturation of cement followed by prolonged absence of water affects the amount of water retained in cement pores, causing cycles of swelling and shrinkage.

- Corrosion of embedded metals—Corrosion products generally occupy a larger volume than the original metals, causing cracking and damage to the concrete-based grout.

- Groundwater leaching—Significant leaching of basic concrete constituents (e.g., calcium, silicon, and aluminum) can reduce the integrity of the grout.

- Chemical attack – Chlorides and sulfates in the soil, waste, or groundwater can attack the concrete by changing the mineralogy of the cement, leading to degradation of the cement.

- Biodegradation—The integrity of the concrete can be challenged if microorganisms can successfully attack the concrete. Important considerations in biodegradation include (1) numbers and types of microorganisms that may attack the concrete, (2) conditions that must exist for these microorganisms to metabolize the grout and grow, especially over time, and (3) resistance of the concrete to these organisms over time.

- Radiation degradation—Concrete materials must be able to withstand high levels of radiation and not sustain damage that will compromise the performance (e.g., formation of stress cracks from gas generation and alteration of mineralogy from bond destruction in molecules) of the grout. The hydrogen may also reabsorb into the concrete or chemically recombine within the concrete. The possibility of hydrogen gas generation from the retained water also could be important if large quantities of the gas are formed and cannot easily diffuse from the waste matrix.

Accurate physical property information is important for understanding and predicting the overall performance of Portland-cement-based grouts. This information can (1) define the range of conditions (such as temperatures and pressures) over which the grout can meet expectations, and (2) provide accurate parameters to use in calculations and modeling. Physical properties are important to all three potential applications of grout at the SDA: immobilization, structural support, and retrieval.

2.1.1 Structural Support Properties

An understanding of the mechanical properties of cementitious grouts is important to ensure adequate structural support of the cap. Compressive strength of the grout is important since the grout will be in compression to support the overlying cap materials. The Code of Federal Regulations specifies the compressive strength of grouted materials for waste disposal be 50 psi (10 CFR 61 1982). The Nuclear Regulatory Commission (NRC) specifies a minimum compressive strength of 60 psi and recommends that the compressive strength of hydraulic cements be 3.45 MPa (500 psi) or greater (NRC 1991). Most Portland-cement-based grouts meet the NRC recommendation and CFR and NRC requirements for the soil and waste loadings of interest. The long-term stability of compressive strength and other grout physical properties will depend on changes that would result from chemistry and the physical degradation discussed above.

2.1.2 Contaminant Migration Indicators

The capability of the grout to prevent migration of contaminants in the SDA will depend strongly on the grout's permeability to water. Hydraulic conductivity and porosity are important indicators of the potential to transport water and contaminants. Rates at which key contaminants leach from mixtures of the grout and waste also provide a good indication of the capability of the grouts to immobilize contaminants. Understanding the potential for formation of fractures in the grout is also important because cracks provide preferential paths for water and contaminants to migrate.

3. DESCRIPTION OF COMPOSITION OF PORTLAND-CEMENT-BASED GROUTS

Portland cement is a hydraulic cement (i.e., an inorganic material or mixture of inorganic materials that sets and develops strength by reacting with water to form hydrates and also forms a water-resistant product) that consists primarily of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate (ASTM C150). The costs of Portland-cement-based grouts were estimated so decision makers can compare these grouts with one another and with other grouts that may be considered. These costs are only rough order of magnitude because the total quantities required depend on current and future decisions. The low cost and wide availability of this cement, combined with its general strength and durability, have made it a natural candidate for grouting a wide variety of waste materials. When used in jet grouting, Portland-cement-based grouts are primarily cement paste because aggregate of any appreciable size causes plugged orifices in the grouting equipment.

3.1 General Portland-Cement-Based Grouts

Portland cements with differing properties are produced to cover the broad range of concrete applications. Property variations result from variations in the composition of raw materials and variations in the manufacturing process (e.g., burning temperature). All Portland cements have the same constituents, but proportions or details of the manufacturing process may vary. Of the five main types of Portland cement currently recognized in the United States, only two have been demonstrated as compatible with jet grouting: Type I and Type H. The following list details both types of Portland cement:

- Type I Portland cement—a general purpose cement that is used when the special properties of the other four types are not required. Typical examples are concrete blocks, floors, reinforced frames, beams, and slabs. This cement has been shown to be successful in jet grouting assessment testing.

- Type H Portland cement—a specialty cement used by the petroleum industry at elevated temperatures and pressures for sealing oil wells. This cement has high-sulfate resistant properties similar to Portland Type V cement and has been shown to be successful in jet grouting assessment testing.

When used as a binder, Portland cement may be blended with additives intended to modify the properties of the final waste form. Some additives—used to improve the workability or enhance the physical, chemical, or cost performance of the Portland cement—are summarized in the following subsections.

3.1.1 Additives for Workability

Additives for workability include:

- Retarding additives—used to delay the setting time for the grout. Many retarding additives also act as water reducers, which can result in a stronger cement.

- Air-entraining additives—used when grout is exposed to freezing and thawing and to deicing salts. These additives entrain microscopic air bubbles that allow space for water to expand during freezing.

- Water-reducing additives—reduces the amount of water needed in the grout. Lower water-cement ratio will increase strength. Most water reducers decrease the needed water by 5 to 10% although expensive, high-range reducers can result in even smaller water requirements.

- Viscosity-reducing additives—used in situations where the cement may be pumped relatively long distances, or where voids are undesirable and removing them through mechanical or other means is difficult. Grouts used in jet grouting must have relatively low viscosities.

These additives may introduce organic compounds that need to be evaluated for use with radioactive waste when radiation fields are expected to be high, since organic compounds can release gases such as hydrogen and carbon dioxide when exposed to radiation fields.

3.1.2 Additives for Physical, Chemical, or Cost Performance

Additives for physical, chemical, or cost performance include:

- Fly ash—decreases permeability, increases mixture fluidity, and lowers initial heat evolution. When added to Portland cement, a pozzolanic fly ash will generate hydrated calcium silicate, which is more amorphous, contains more aluminate, and has a calcium-silicon ratio lower than ordinary Portland cement.

- Blast furnace slag—decreases permeability, lowers internal solution oxidation-reduction potential, lowers initial heat evolution, increases mixture fluidity, and helps retain mobile species, especially reducible species. Blast furnace slag is also a hydraulic material that is activated in cement to produce hydrated compounds with low calcium-silicon ratios and sulfoaluminates.

- Silica fume—decreases permeability and increases sorption of metals and nonmetals. Its hydration in a Portland cement blend will produce Type III calcium silicate with a very low calcium-silicon ratio.

- Sodium silicate—precipitates heavy metals, decreases permeability, increases strength, and hastens the set in the presence of pozzolans, ashes, and fumes. It produces calcium silicate by capturing the calcium ions released by the hydrolysis of cement.

- Calcium hydroxide and sodium hydroxide—conditions borate and sulfate waste and other waste species, which can be precipitated to form insoluble or inoffensive compounds better suited for the final waste form, and hastens the set in the presence of pozzolans, ashes, and fumes.

- Sodium sulfide and thiosulfate – reduce leaching of RCRA metals.

Although the effect of individual additives can be given in general terms, using more than one additive or using additives with some waste forms may result in complex reactions that are difficult to initially predict. Therefore, using multiple additives and expected waste form development both heavily rely on an empirical approach.

3.2 Commercially-Available Portland-Cement-Based Grouts

Three commercially-available Portland-cement-based grouts have properties compatible with jet grouting and have been tested in past grouting studies. These grouts have proprietary ingredients, including the following:

- GMENT-12 was developed specifically for jet grouting applications based on a tank closure grout initially developed by the Savannah River Site. The grout is comprised of American Society for Testing and Materials (ASTM) International Type V Portland cement, blast furnace slag, and silica fume. This grout has acid-base properties (pH) of about 9 following set and cure, and creates a reducing environment in waste site groundwater. GMENT-12 was specifically developed to immobilize uranium, plutonium, and other actinides (Loomis et al. 2002).

- TECT HG and TECT are pozzolanic cementitious grouts with proprietary additives from Carter Technologies. They have a low heat of hydration and were formulated to tolerate and stabilize small amounts of organic contamination. These grouts have a longer setting time than Portland cement slurries. The setting time is on the order of 1 day when mixed with soil. As the grouts cure, the pH first rises to about 12 and then falls to below 9 over time. TECT 1 exhibited good performance in previous studies, and the HG version of TECT, which was specifically formulated for stabilization of waste containing mercury, was used for the INL Site Acid Pit Project in the SDA (Loomis et al. 1999).

- U.S. Grout is a pozzolanic cement from Hess Products of Malad, Idaho. This grout is a mixture of Type H Portland cement and local Idaho pumice that exhibits physical properties (i.e., low viscosity and delayed set parameters) that are compatible with jet grouting (Loomis et al. 2002).

3.3 Specialty Grout Developed for the U.S. Department of Energy

The following Portland-cement-based grout was developed at the Savannah River Site for stabilizing aqueous nitrate salt waste streams with their radioactive contaminants:

- Saltstone is comprised of blast furnace slag, fly ash, and small amounts of Portland cement. This grout has a pH of about 9 after set and cure, and creates a reducing environment in waste site groundwater. Saltstone was specifically designed to stabilize technetium and plutonium (Loomis et al. 2002).

4. AVAILABLE INFORMATION ON CEMENTITIOUS GROUT PERFORMANCE

Information has been gathered on the performance of Portland-cement-based grouts under conditions typical of those expected at the SDA to address the grout performance characteristics discussed in Section 3. This information was assembled from an extensive literature search, results of jet grouting tests at the INL Site, and information from tests on grouts now being carried out at the INL Site.

4.1 Effects of the Chemistry of Portland Cement

Long-term performance of cement may degrade because of changes in basic cement chemistry or outside influences that cause changes in the chemistry. Chemistry and associated performance data are not available for Portland cement beyond about 150 years because it was not in use. The complexity of Portland cement basic chemistry and the lack of long-term data make modeling difficult and result in large uncertainties in predicted long-term behavior. As a result, there are uncertainties in the long-term durability of Portland-cement-based grouts.

4.1.1 Basic Chemistry of Portland Cement

In terms of cement-based grout performance, understanding of both short-term and long-term chemical reactions is necessary to predict how the grout will perform in an application at the SDA. Short-term reactions deal with the cure of the cement paste and chemical integration of waste components into the paste. Long-term reactions deal with chemical reactions of the grout from environmental exposure and reaction of incorporated materials, such as aggregate and encapsulated metals.

4.1.1.1 Short-Term Reactions. Short-term reactions of Portland cement are primarily related to the hydration, or cure, of freshly cast grout. The hydration mechanisms of cement pastes are a complex series of chemical reactions, dissolutions, precipitations, exchanges, and crystallizations, which can be disturbed in many different ways (Mattus and Gilliam 1994).

Four main chemicals in concrete—tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite—are responsible for cure reactions as follows:

- Tricalcium silicate ($3CaO{\bullet}SiO_2$, also abbreviated C_3S)—hydrates and hardens rapidly, and is responsible largely for the initial set and early strength

  $2(3CaO{\bullet}SiO_2) + 6H_2O \rightarrow 3CaO{\bullet}2SiO_2{\bullet}3H_2O + 3Ca(OH)_2$

- Dicalcium silicate ($2CaO{\bullet}SiO_2$, also abbreviated C_2S)—hydrates and hardens slowly, and largely contributes to strength increases at ages beyond 1 week

  $2(2CaO{\bullet}SiO_2) + 4H_2O \rightarrow 3CaO{\bullet}2SiO_2{\bullet}3H_2O + Ca(OH)_2$

- Tricalcium aluminate ($3CaO{\bullet}Al_2O_3$, also abbreviated C_3A)—liberates a large amount of heat during the first few days and contributes slightly to development of early strength

  $3CaO{\bullet}Al_2O_3 + 12H_2O + Ca(OH)_2 \rightarrow 3CaO{\bullet}Al_2O_3{\bullet}Ca(OH)_2{\bullet}12H_2O$
  $3CaO{\bullet}Al_2O_3 + 10H_2O + CaSO_4{\bullet}2H_2O \rightarrow 3CaO{\bullet}Al_2O_3{\bullet}CaSO_4{\bullet}12H_2O$

- Tetracalcium aluminoferrite ($4CaO{\bullet}Al_2O_3{\bullet}Fe_2O_3$, also abbreviated C_4AF)—hydrates rapidly, but does not contribute much to development of strength

  $4CaO{\bullet}Al_2O_3{\bullet}Fe_2O_3 + 10H_2O + 2Ca(OH)_2 \rightarrow 6CaO{\bullet}Al_2O_3{\bullet}Fe_2O_3{\bullet}12H_2O$.

Each of the hydration reactions is exothermic (i.e., each produces heat during the curing process). Many factors influence the heat generated during cure, including the fineness of the cement, the amount of water available, and the chemical ratios of C_3S, C_2S, C_3A, and C_4AF. Other factors also may influence the amount of heat produced during the hydration reaction, including interactions with the aggregate, presence of chemicals that inhibit or stop the reaction, and organic materials that prevent coating and

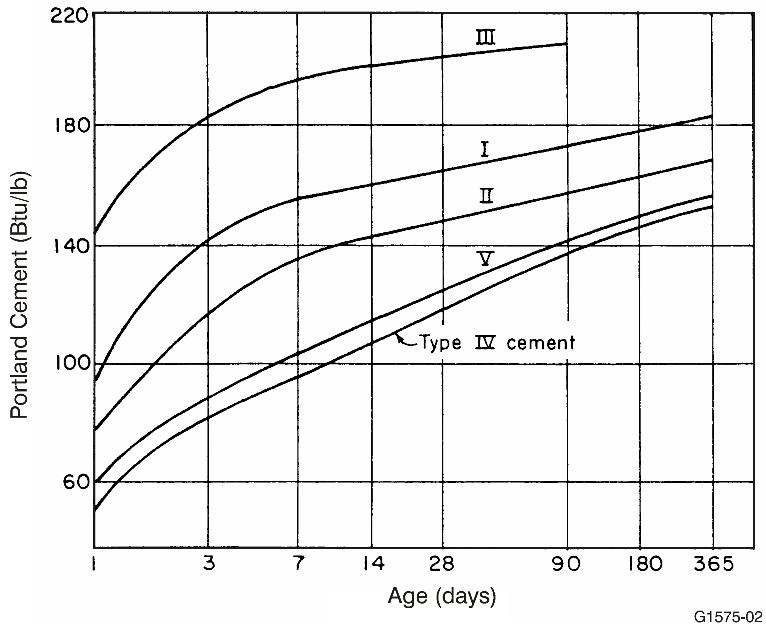

Figure 7. Typical heat of hydration curves for various types of cement.

bonding of particles. Figure 7 (Kosmatka and Panarese 1994) illustrates typical heats of reaction for common types of Portland cement.

4.1.1.1.1 Effect of Chemical Reactions on Grout—In a review of cement-based immobilization at U.S. Department of Energy sites, Mattus and Gilliam (1994) found that dealing with mixtures of many waste species created significant complexity. Many chemical species have been demonstrated to have an effect on the cure reactions of grout. Mattus and Gilliam present the ranking of common anions and cations, which can be accelerators or retarders of Portland cement as follows:

Cations:

$Ca^{2+} > Ni^{2+} > Ba^{2+} > Mg^{2+} > Fe^{3+} > Cr^{3+} > Cu^{2+} > La^{3+} > NH^{4+} > K^{+} > Li^{+} > Cs^{+} > Na^{+}$

←--------------------Acceleration

Retardation--------------------------→

$Cu^{2+} > Zn^{2+} > Pb^{2+}$

Anions:

$OH^{-} > Cl^{-} > Br^{-} > NO_3^{-} > SO_4^{2-} > CH_3CO_2$

←----------------------Acceleration

Note that cations and anions always exist in charge balance, so it is not always possible to determine if any given combination will result in acceleration or retardation of the cement hydration process. Certain chemicals are known to accelerate or retard the cure of cement and are briefly discussed below.

*4.1.1.1.2 Accelerating Admixtures—*Calcium chloride is the most widely used cement accelerator and has been demonstrated to primarily affect the C_3S hydration reaction. Most inorganic electrolytes, especially soluble calcium salts, accelerate the C_3S hydration reaction. Aqueous solutions of various chlorides—such as calcium, aluminum, and sodium and alkali carbonates, aluminates, and silicate—also have been demonstrated to accelerate the C_3S hydration reaction. A few organic compounds are known to be accelerators of C_3A hydration, among which triethanolamine is the most well known and often used commercially (Mattus and Gilliam 1994).

*4.1.1.1.3 Retarding Admixtures—*Many chemical species can retard the set of grout. Organic compounds known to retard grout set include phenols, glycols alcohols, carbonyl, carboxilate, chlorinated hydrocarbons, oil, and grease. Inorganic compounds known to retard grout set include sodium salts of phosphoric, boric, and oxalic acids; some chloride salts; and some heavy metals, such as copper and zinc. Chromate, sulfate, and carbonate salts also can retard the set of grout (Mattus and Gilliam 1994).

4.1.1.2 Long-Term Reactions. Long-term reactions that can have a serious effect include compounds that have an expansive reaction with components in the grout. These long-term reactions create spalling (i.e., surface flaking of cement) of the grout surface and seriously degrade the grout. Steric acid has been demonstrated to rapidly deteriorate grout, while compounds such as ethylene glycol, acetic acid, butyric acid, formic acid, lactic acid, citrate, oxalate ethylene diaminetetraacetic, and sugar have been demonstrated to slowly deteriorate grout. Sodium and potassium chloride in concentrated solutions also have been demonstrated to deteriorate grout. Cracking and spalling also can occur as a result of the formation of expansive ettringite when grout is exposed to sulfate-rich materials (Mattus and Gilliam 1994).

4.2 Effects of Physical Interactions and Other Interactions

Physical and biological interactions will occur in the SDA that also can influence the chemical and physical behavior of the grouts. Examples of interactions that could reduce grout durability, and the effect of the conditions in the SDA on these interactions are discussed in the following subsections.

4.2.1 Freeze-Thaw Cycles

Freezing of Portland-cement-based grouts can cause the water in the pore spaces to expand, causing the potential for damage to the material structure. Repeated freezing and thawing of grouts over a prolonged period can result in three types of defects in a cement-based grout: spalling, scaling, and cracking. Spalling is a definite depression caused by separation of surface concrete. Scaling occurs to a depth of 2.5 cm (1 in.) from the surface resulting in local peeling or flaking. Cracking varies in depth and length. All of these defects are undesirable for a durable grout.

The upper surface of the waste in the SDA is located about 0.9 m (3 ft) below the surface and is in a layer 0.9 to 4.9 m (3 to 16 ft) thick. This upper surface will be 0.9 to 2.7 m (3 to 9 ft) deeper once a cap is installed. Jet grouting is expected to place the cementitious grout more than 1.8 m (6 ft) below the surface. Figure 8 (Pitman 1989) shows the temperatures during late 1985 and all of 1986. These temperatures are considered typical of what is expected in the SDA. Temperatures at 2.1 m (6.9 ft) never dip below about 4°C (39°F), which is well above freezing. Temperatures at lower levels show less variation and range between 6.7 and 12.2°C (44 and 54°F). Based on these results, damage from freeze-thaw cycles is not expected for the cementitious grouts used in the SDA.

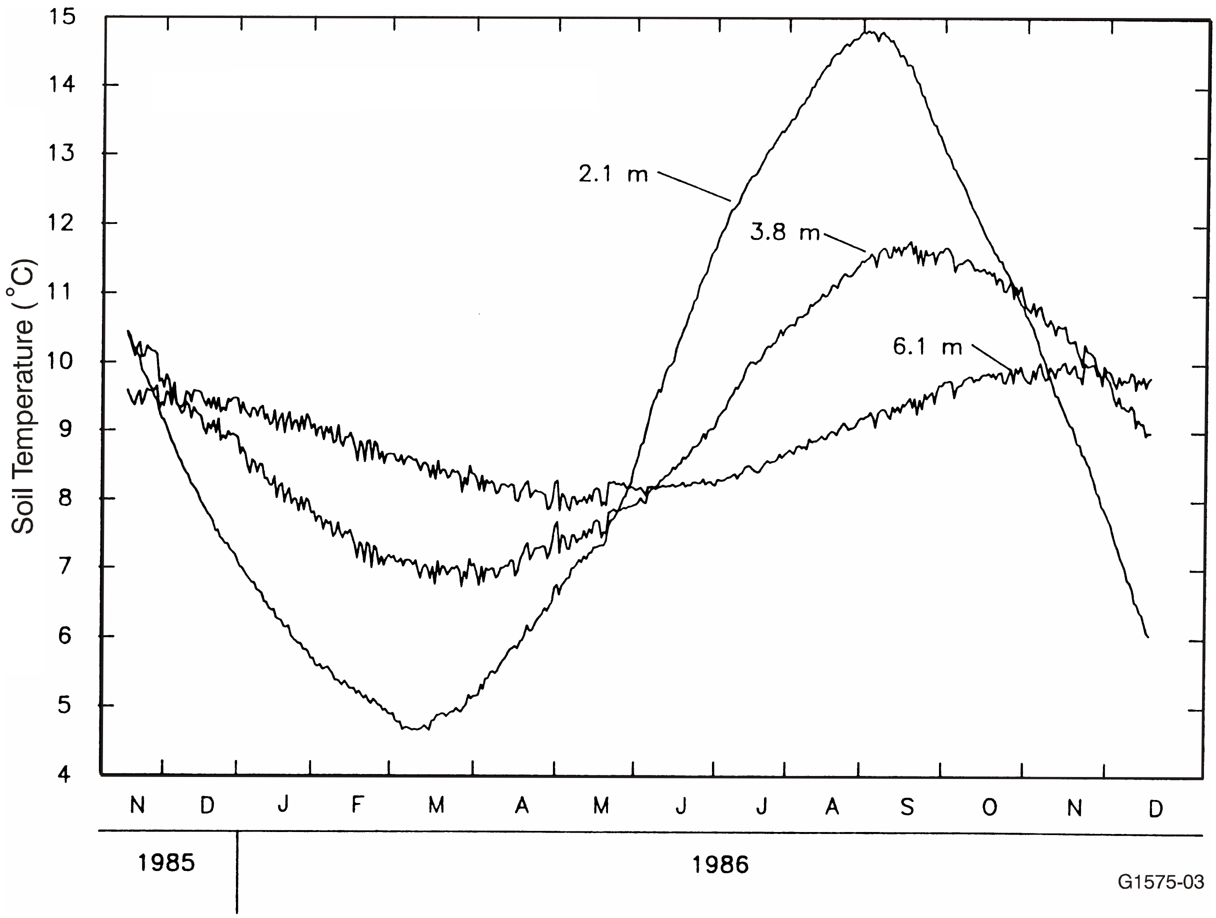

Figure 8. Variation of soil temperature with depth and time at the west test trench.

4.2.2 Wet-Dry Cycles

Repeated wet-dry cycles influence the water content of the cement pore space. The volume of the cement paste will vary as its water content varies, shrinking when it is dried and swelling when rewetted to 100% relative humidity. The first drying (to an intermediate water content of about 47% relative humidity) for cement paste is largely irreversible; this irreversible component strongly depends on the porosity of the paste, being smaller at lower porosities and water-cement ratios (Verbeck and Helmuth 1968). The shrinkage-water content relationship appears to depend on the length of time the cement is held in the dried condition (i.e., 47% relative humidity or less). Repeated wet-dry cycles have the potential to result in shrinkage that damages the cement structure.

The water content of soil in the SDA remains relatively constant over the year, depending on depth. Figure 9 shows the water content measured at different depths of three different times of the year for a location considered typical of the SDA (Pitman 1989). At locations more than 2 m (6.6 ft) below the surface, water content remains relatively constant. Variations of this magnitude in water content are not expected to result in sufficient variation in wetting and drying to cause damage to cementitious grout.

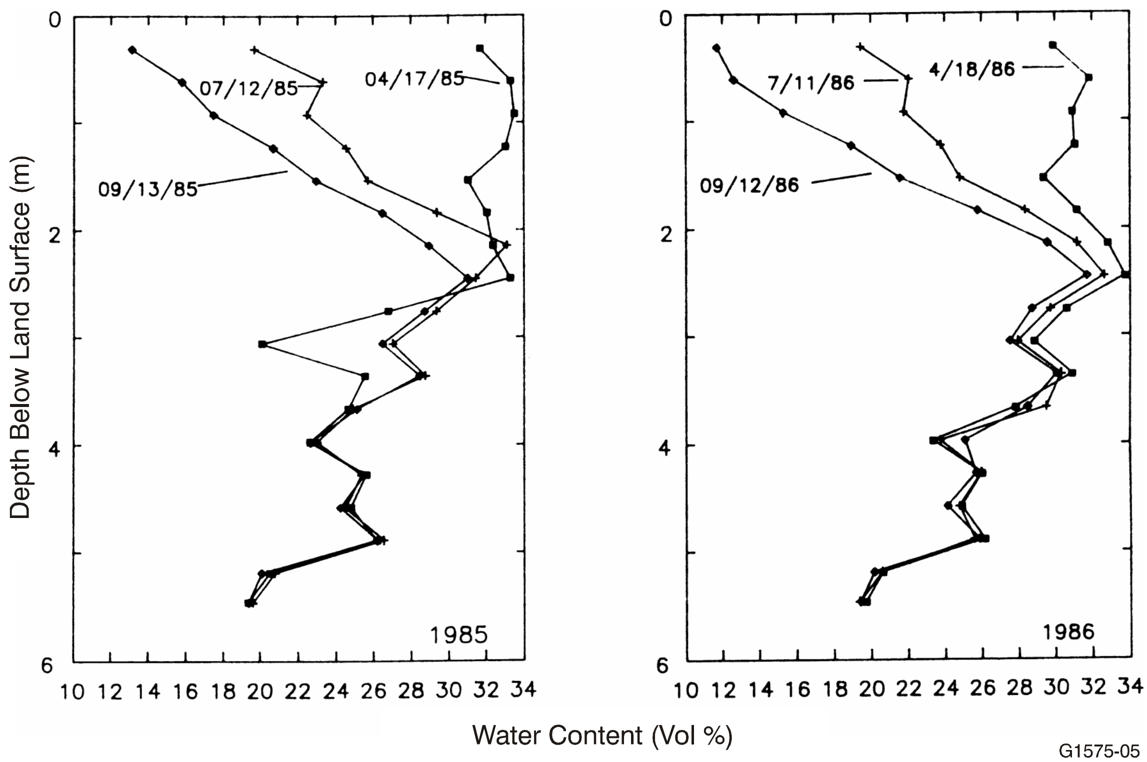

Figure 9. Variation of soil-moisture content with depth and time at Neutron-Probe Hole 1.

4.2.3 Corrosion of Embedded Metals

The four major metals of interest with respect to corrosion in the SDA are carbon steel, stainless steel, inconel, and beryllium. Corrosion of metal is a concern in two ways. First, the products of corrosion from metal take up more volume than the original metal, leading to localized regions of stress within cement near the encased metal. Eventually, the stress may exceed the tensile strength of the cement and cause cracks. Cracks can increase the effective hydraulic conductivity of the cement, which, in turn, can enhance the corrosion rate of the metal and the mobility of contaminants within the cement (Clifton and Knab 1989). Second, the metal may contain contaminants. As the metal corrodes, contaminants can be released from the metal. Both mechanisms are of interest in the SDA.

Although formation of cracks in cement-grouted regions of the SDA is assumed, cements that are reinforced or contain fiber are generally more resistant to external stresses—such as differential loading and settling—and also form few cracks during curing. The presence of metal in the cement can improve tensile strength of the cement; this is the basis for inclusion of rebar and metal pieces in commercial concrete structures. Some of the metal in the SDA could act like rebar in grouted regions of the waste.

Because of the use of steel in commercial construction, a lot of information about corrosion of carbon steel, especially rebar, in concrete is available in the literature. Studies of stainless steel are also available because it is used for reinforcing some commercial construction. Inconel and beryllium are not used for reinforcing, and no data could be located on their behavior in concrete. However, it is known that beryllium is vigorously attacked by aqueous alkaline solutions, and, before setting, Portland cement is essentially an aqueous alkaline solution with a pH of 12 (Miller and Boyd 1967).

Corrosion of steel in concrete has been studied extensively (Hansson and Sorensen 1990; Al-Tayyib et al. 1990; Videm 2001; Jiang, Liu, and Ye 2004; Novak, Mala, and Joska 2001; Soleymani and Ismail 2004; Gonzalez, Miranda, and Feliu 2004; Saremi and Mahallati 2002; Hou and Chung 2000; Trejo and Monteiro 2005). The high pH of concrete (pH is greater than 12.5) makes rebar passive by allowing a protective layer to develop on the surface layer of the steel, protecting it from corrosion (Clifton and Knab 1989; Veleva et al. 2002). The corrosion rate of carbon steel is slow while the protective layer is intact, approximately 0.1 µm/year (Hansson and Sorensen 1990; Novak, Mala, and Joska 2001). Corrosion of steel in concrete requires both oxygen and water, and this process is generally slow when other agents, such as chloride, are not present (Clifton and Knab 1989; Yoo et al. 2003). The most studied mechanism for the initiation of corrosion of steel in concrete is the diffusion of chloride ions through the concrete (Hansson and Sorensen 1990; Al-Tayyib et al. 1990; Videm 2001; Jiang, Liu, and Ye 2004; Veleva et al. 2002).

Chloride is a major agent of attack of carbon steel within concrete (Soleymani and Ismail 2004; Hansson and Sorensen 1990; Novak, Mala, and Joska 2001; Al-Tayyib et al. 1990; Clifton and Knab 1989; Yoo et al. 2003). Waste in the SDA contains some chloride salts, but not in the concentrations encountered by bridges, roadbeds, and structures. Chloride ions disrupt the protective passive layer on rebar and allow corrosion to start. The rate of corrosion when chloride disrupts the passive film is several orders of magnitude higher (1.23 to 1.68 µm/year [Al-Tayyib et al. 1990], 1 to 65 µm/year [Novak, Mala, and Joska 2001], and 67 to 111 µm/year [Trejo and Monteiro 2005]) than with an intact passive film (Hansson and Sorensen 1990; Al-Tayyib et al. 1990; Videm 2001; Novak, Mala, and Joska 2001; Yoo et al. 2003). The rate of corrosion depends on test conditions, including cement formulation, chloride concentration, and mechanism of delivery, temperature, and hydration. In general, higher concentrations of chloride result in faster corrosion rates for carbon steel (Saremi and Mahallati 2002). The main problem with rebar corrosion is not loss of strength of the rebar, but formation of cracks in the concrete. The products of corrosion require more volume than the original rebar, leading to cracking near the rebar, which, in turn, leads to enhanced transport of water and chloride. In the SDA, cracking of grout from corrosion of metal could result in cracking and preferential pathways for water migration through the grout. For ordinary Portland cements, chloride concentrations less than 0.4 wt% are low risk, concentrations 0.4 to 1 wt% are moderate risk, and concentrations greater than 1 wt% are high risk for steel corrosion (Andion et al. 2001).

Surface conditions and the type of steel also can influence the steel corrosion rate in concrete. Studies have examined the effect of the initial surface condition (e.g., rough, smooth, prerusted, or precleaned) of the rebar on the corrosion rate of the rebar (Hansson and Sorensen 1990; Al-Tayyib et al. 1990; Novak, Mala, and Joska 2001). Conclusions from these studies are mixed; some have found that the presence of rust on carbon steel before grouting has no effect or even improves corrosion resistance (Hansson and Sorensen 1990; Al-Tayyib et al. 1990), while others have found that the presence of rust increases the rate of corrosion (Novak, Mala, and Joska 2001). The type of steel placed in concrete will affect its resistance to corrosion. For example, ASTM A706 low-alloy reinforcing steel was found to be less corrosion resistant than ASTM A615 regular reinforcing steel (Trejo and Monteiro 2005). Stainless steel has been studied for use in concrete, which will be exposed to high chloride (bridges) or sulfate (marine piers) concentrations. Stainless steel is of interest because of its ability to regenerate a passive layer, and initial laboratory studies indicate that stainless steel is more resistant to corrosion than carbon steel in chloride or nonchloride environments (Veleva et al. 2002; Andion et al. 2002).

Water content and formulation of cement also affect the corrosion rate of steel in concrete. Increasing the ratio of water-to-cement increases the porosity of the cement (Hansson and Sorensen 1990; Clifton and Knab 1989), making the concrete more susceptible to chloride infiltration. Various additives for cement, including fly ash, silica fume, latex, and carbon fibers, have been studied to evaluate their potential to reduce the corrosion rate (Hou and Chung 2000; Ampadu and Torii 2002; Hansson and Sorensen 1990). The composition of fly ash depends on its source. In general, the fine particulate size combined with chemical interactions results in cements with lower permeability. Calcium oxide in fly ash provides cementing and pozzolanic[d] activity. Aluminium oxide and iron oxide provide pozzolanic activity. Fly ash (3 to 22 wt%) can reduce the porosity of cement and the transport of chloride through the cement (Hansson and Sorensen 1990; Ampadu and Torii 2002).

Carbonation, caused by diffusion into and reaction with the cement minerals, decreases the pH of the cement, which can then lead to destruction of the protective passive film and corrosion of steel in concrete. The rate of carbonation of concrete depends on the composition of the cement, the degree of saturation, and the concentration of carbon dioxide, among other factors (Jiang, Liu, and Ye 2004; Andion et al. 2001). The rate of carbonation of concrete is expected to be slow in the SDA, and the carbonation front (defined as a pH of 9) is expected to penetrate concrete in the SDA at a rate of 7.34×10^{-2} mm/year (see the discussion in Section 4.2.7).

4.2.4 Leaching of Basic Cement Constituents

The structural and hydraulic integrity of cementitious grouts could be compromised if the basic chemical constituents are leached by infiltrating water, such as groundwater. Several candidate grouts were tested to assess the leach behavior for key grout constituents, including calcium, silicon, and aluminum (Loomis et al. 2002). Strontium carbonate and sodium nitrate were added to the grout at 0.1 wt% to act as tracers that could be monitored during leaching.

The leach testing protocol in ANSI/ANS 16.1 was used for all constituent leach testing. Neat grout samples of GMENT-12, TECT HG, U.S. Grout, and Saltstone were immersed in a series of demineralized water baths for specified times over a 90-day period. All leachate samples were analyzed for calcium, silicon, aluminum, strontium, and nitrate using inductively-coupled plasma spectrometry. Three replicate sets of leach tests were performed for each grout. Average leachability indices and diffusivity coefficients were calculated for each replica set.

Table 1 shows the leach index results for the grout specific constituents (i.e., calcium, silicon, and aluminum) and for the two tracers. A higher leach index indicates lesser amounts of constituents leached and the likelihood of increased durability of the grout. All grouts exhibited relatively high leach indices for the constituents tested, with leach indices of U.S. Grout slightly lower than the remainder of the grouts.

Table 1. Average leach index for grout constituents for neat grout.[a]

Grout	Calcium Leach Index	Silicon Leach Index	Aluminum Leach Index	Strontium Leach Index	Nitrate Leach Index
GMENT-12	10.5 ± 0.5	10.7 ± 1.1	12.2 ± 0.8	10.0 ± 0.5	10.4 ± 0.6
TECT HG	10.15 ± 0.5	11.1 ± 0.5	12.3 ± 0.5	10.1 ± 0.3	11.0 ± 0.7
U.S. Grout	9.8 ± 0.9	10.2 ± 0.7	11.1 ± 0.4	10.6 ± 0.9	9.2 ± 0.3
Saltstone	10.5 ± 1.0	10.2 ± 0.9	12.6 ± 0.9	10.2 ± 0.6	10.8 ± 0.8

a. Results reported ± one standard deviation.

An estimate of the rate of grout erosion caused by leaching of the important constituents was computed based on the leach test results used to develop Table 1 (Loomis et al. 2002). These calculations assumed an average water infiltration rate in the SDA of 8.5 cm/yr (3.3 in./yr) and a 2-m (6.6-ft) thickness

d. Pozzolanic materials do not directly act as cement, but they are capable of reacting chemically with calcium hydroxide at ordinary temperatures to form compounds with cementitious properties.

for a pure grout monolith. Based on these assumptions, the time required for 1% dissolution of calcium, silicon, and aluminum from the grout was calculated to be in the range of "tens of thousands of years" (Loomis et al. 2002). For example, calculations for GMENT-12 estimated 39,000 years for a 1% loss of calcium; 16,300 years for a 1% loss of silicon; and 150,000 years for a 1% loss of aluminum. All of the tested grout materials had similar constituent loss rates. These long timeframes indicate that leaching alone should not result in degradation of the tested grouts within at least the first thousand years.

4.2.5 Radiation-Induced Degradation

Grout will be exposed to radiation emanating from the waste. This radiation has the potential to degrade the performance of the grout by damaging the basic chemical and physical structure. Evaluating the potential radiation damage requires three key pieces of information. First, radiation damage limits must be identified for cementitious material based on experimental evidence from reliable sources. Next, a desired time frame over which the irradiation takes place must be established. Then, the dose to the grout must be estimated based on the contribution of expected radiation sources over the irradiation time.

There is historical evidence that concrete is durable when exposed to high radiation levels for long time periods because it has been used as shielding in nuclear reactors, hot cells, and related nuclear facilities for over half a century. During the early period of nuclear energy development, extensive studies were conducted to examine the effects of various types of radiation on concrete to ensure that structures and enclosures would remain viable over desired lifetimes. A brief discussion of results from these studies is presented initially to identify upper bound radiation damage levels for cementitious materials. These results are followed by a discussion of possible levels of radiation in the SDA and the relationship of these levels to the potential for damage to the cementitious grout. A span of 1,000 years is assumed to be a reasonable time frame over which the grout should remain functional; this is based on some recent preliminary cap design analyses prepared for the SDA (Mattson et al. 2004).

4.2.5.1 Radiation Effects on Cement. In many materials, exposure to radiation will change the crystal lattice and deteriorate the lattice order. These changes to the crystal structure can lead to a decrease in the structural performance of the material. At high radiation levels, significant energy may also be deposited in the material as the radiation is absorbed. Depending on the timeframe and the thermal characteristics of the material, the local material temperature may increase to levels in which thermal damage is possible.

Cement has been exposed to a wide range of radiation sources, including neutrons and alpha, beta, and gamma radiation. Although neutrons have been shown to cause concrete damage at relatively high exposure levels (integrated neutron fluxes exceeding about 5×10^{18} n/cm^2 [Kaplan 1983]), neutron fluxes in the SDA are negligible and damage to the grout from neutrons will not be considered further. The SDA contains a large inventory of radionuclides that produce alpha particles. Alpha particles have a high energy spectrum, but will not penetrate a piece of paper. When encapsulated in grout, alpha particles could cause localized damage at the cement surface. However, this damage should not cause significant grout failure because the depth of damage would be minimal.

Beta radiation is more penetrating than alpha but can be shielded by about 0.6 cm (1/4 in.) of aluminum. Damage in concrete would be contained within about 2.5 cm (1 in.) of the point of contact between the concrete and the beta-emitting material. This localized damage would not be expected to compromise the grout performance.

Gamma radiation can penetrate several feet of cement; damage from gamma irradiation of cement has been shown in various studies. The effect of gamma irradiation on the compressive strength of concrete appears to be complex. A high level summary of both neutron and gamma irradiation studies is presented by Kaplan (1983). Alexander's results are typical of many studies (1963), in that he reported no reduction in compressive strength of concrete for gamma radiation doses up to 10^{10} R, when compared to the strength of specimens that had not been irradiated or heated. (Some researchers postulate that some loss of strength results from relatively high temperatures that occur during studies with high irradiation levels.) Sommers (1969) observed no reductions in compressive strength at 1.2×10^{10} R but found reductions in compressive strength ranging from 25 to 60% for radiation doses of about 2×10^{11} R. For these tests, the specimens were immersed in demineralized water to shield them from neutrons. Both irradiated and unirradiated specimens were covered with water to expose the specimens to similar conditions. The water combined with radiation seems to have increased the degradation of the concrete, because other studies that combined both neutron and gamma radiation—but without the effects of water—have not shown such large decreases in compressive strength. Sommers results indicate a general reduction in compressive strength for concrete between 10^{10} and 2×10^{11} R.

More recent studies at Brookhaven National Laboratory (Soo and Milian 2001) provide data indicating that the damage limit is lower than the 10^{10} R limit derived from the earlier testing. These tests evaluated the effect of irradiation rate on compressive strength to examine a lower rate that would be more typical of what might be expected for waste. Portland Type I, Portland-Type-V, and Portland-Type-V cements with 15 wt% silica fume were tested. Standard Ottawa sand was used in place of aggregate, making the test material similar to jet grouting material. Two and a half-cm (1-in.) cubes were produced and irradiated in the air at 10°C (50°F) with Co-60 gamma fluxes of 3.1×10^3 and 3.8×10^7 R/hr. Control samples (unirradiated) were made at the same time and held at 10°C (50°F) and at room temperature (about 20°C [68°F]). Periodically, two irradiated specimens were removed and compressive strength was tested. Three to five unirradiated samples were tested at the same time. Figure 10 shows results from the irradiation studies for Portland Type I cement mortar in terms of percent of unirradiated compressive strength. These results indicate that irradiation at a lower level (3.1×10^3 R/hr) resulted in an earlier reduction in compressive strength than the higher irradiation level. These results would indicate compressive strength could begin to degrade at integrated irradiation levels as low as 10^7 R, as compared with 10^{10} R from earlier studies.

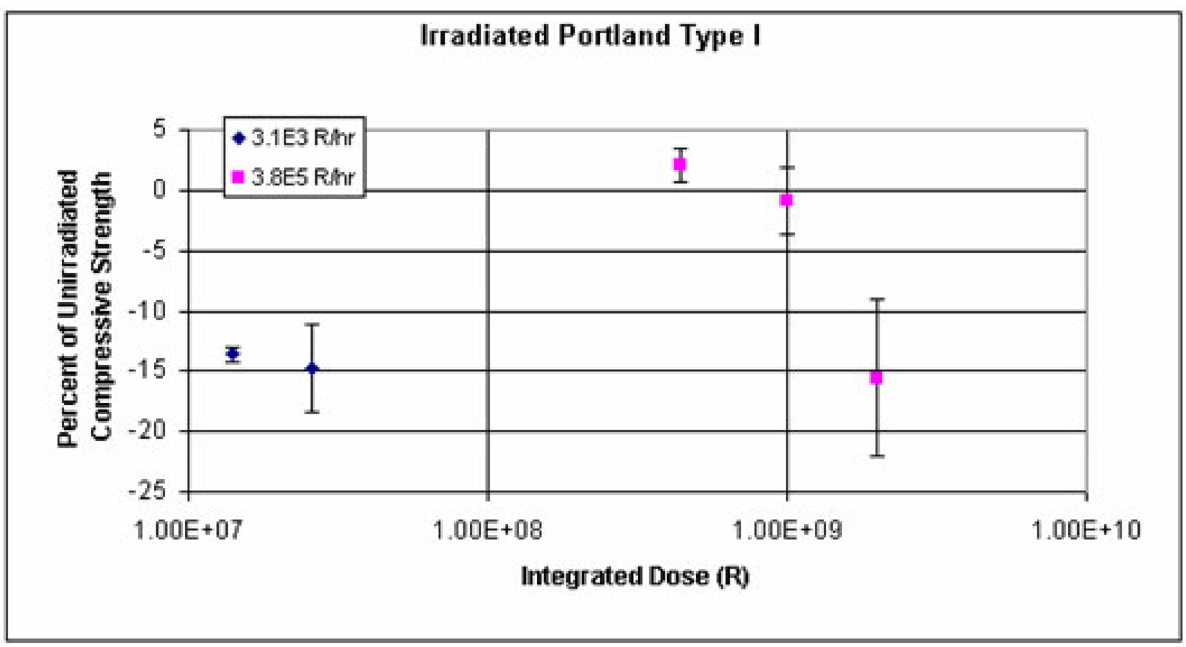

Figure 10. Percent of unirradiated compressive strength for samples irradiated at higher and lower R/hr (Soo and Milian 2001).

Figure 11 shows the Portland Type I cement mortar data plotted against the days over which the specimens were irradiated. A correlation seems to appear between the number of days the samples were irradiated and a decrease in compressive strength. For the Portland Type I cement mortar, the decrease in strength appears to indicate a final strength loss of about 15%. The other two Portland cement mortars tested show losses in compressive strength of about 27%, without achieving a stable minimum strength value after one year. Soo and Milian (2001) conclude:

> "It was shown that the curing time during the radiation is an important factor in quantifying the amount of strength loss. It is proposed that the actual mechanism for irradiation-induced losses in strength is connected with the loss of water of hydration from the cement. For a given dose level, a slower dose rate will cause a larger loss in compressive strength. For a dose rate on the order of 3×10^3 R/hr, losses in strength may occur for relatively low doses in the 10^7 R range."

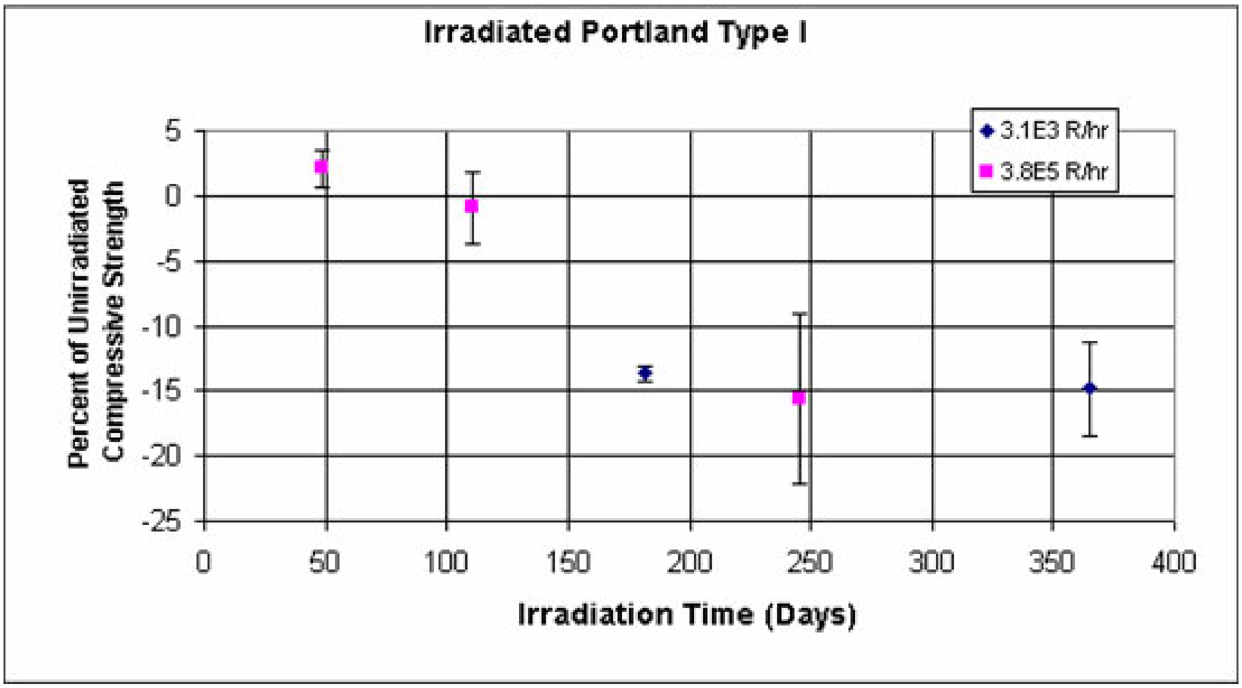

Figure 11. Relationship between percent of unirradiated compressive strength and days irradiated for both irradiation rates (Soo and Milian 2001).

The reasons for the differences between the results of Soo and Milian and previous concrete testing are difficult to understand fully. Trends shown in Figure 11 would require additional data for both irradiation levels to ensure that the trends shown are correct. In addition, there should be reasonable agreement between test results from the higher irradiation rate (3.8×10^5 R/hr) and results from testing performed by others. Degradation in compressive strength appears to begin at about 2×10^9 rad for Portland Type I cement mortar for the Soo and Milian tests, as compared to values in excess of 1×10^{10} rad for other experimenters. Further testing will be necessary to understand whether these differences result from the causes proposed or whether they are a result of testing anomalies (e.g., small specimen size, procedures, and equipment) from other causes.

The effect of gamma radiation on the tensile strength of concrete was evaluated through testing of both irradiated and unirradiated concrete specimens. Gray's (1972) results showed that at a gamma dose between 2 and 4×10^{10} R there was no significant decrease in concrete tensile strength.

Gas is generated when concrete is exposed to gamma and neutron radiation (Gray 1972, Kelley et al. 1969) through radiolysis of water that is associated with the concrete. Generated gas species consist primarily of hydrogen and oxygen. This gas generation is not considered to have a significant effect on the properties of the concrete (Kaplan 1983), but the gases may have a corrosive effect on metals that are close to gas generation sites. Even if corrosion of metal waste materials takes place in a jet grouted area, these metals would continue to be encapsulated by the surrounding grout.

Absorption of nuclear radiation energy by concrete has the potential to increase temperature. Since concrete has a relatively low thermal conductivity, high gamma radiation fluxes may result in increased temperatures. Testing generally used high gamma fluxes to minimize the time required to achieve desired integrated doses. For example, the average gamma source intensity for Sommers' (1969) tests varied from 2.4×10^6 to 3.9×10^6 R/hr. As discussed in the following section, a conservative maximum source intensity for the waste in the SDA is about 100 times smaller (5×10^4 R/hr), leading to the conclusion that the small quantities of energy deposited by the waste will dissipate and temperatures capable of damaging the concrete will not occur.

4.2.5.2 Potential Subsurface Disposal Area Radiation Exposure of Cementitious Grout. If selected for use, cementitious grout will be exposed to various levels of radiation as it comes in contact with the different types of radioactive waste buried in the SDA. There are generally large areas of the SDA where the buried waste has low activity and is dispersed, resulting in an average concentration of radionuclides that is relatively low. However, discrete packages of relatively high activity materials were buried in the SDA pits and trenches over the years. These packages can result in localized concentrations of high radioactivity and dose rates. Understanding the effect of these concentrations on the grout radiation dose is key in evaluating the potential for significant radiation damage to the grout structure. This section develops a set of worst-case estimates of the radiation dose for the pits and trenches and provides a rough order of magnitude estimate of radiation damage.

Shipping records for the SDA indicate that the pits and trenches contain 861 packages with surface radiation dose rates that are above 1 R/hr at the time of disposal (EDF-3543)[e]. Only nine of these packages were disposed of in the pits, with the remainder buried in the trenches. The last remote-handled trench disposal was in September of 1981. After that date, all remote-handled disposals were in the soil and concrete vaults.

Of the 861 remote-handled packages, 67 had surface dose rates of 100 R/hr or greater and 17 had surface dose rates that exceeded 1,000 R/hr at the time of disposal. Table 2 lists those material packages that exceeded 1,000 R/hr at the time of disposal. All dose rates will have decayed based on the radionuclide content. The predominant isotope identified for the packages is Co-60, which has a half life of 5.27 years. Assuming grouting will begin in 2007 and using the 1981 date of the last disposal, the surface dose rates for those packages where Co-60 dominates will be reduced by a factor of about 30 because of radioactive decay. Earlier disposals will have greater reductions. For example, the package with the highest surface dose (150,000 R/hr in 1963) is estimated to have a surface dose of about 460 R/hr in 2007 based on Co-60 decay.

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e. It is recognized that the contents of the waste placed in the SDA continues to be refined as the quality of waste databases is improved. These calculations were done with the most current information available at the time of these calculations. It is recommended that, before future calculations are done, the literature be checked to ensure current values are used for the contents of the waste in the SDA.

Table 2. Materials buried in the Subsurface Disposal Area pits and trenches that were identified through shipping records as having the highest direct radiation dose rates.

Disposal Location	Disposal Date	Originating Organization	Activity (Ci)	Isotopes	Surface Dose Rate (R/hr) at Disposal
T28	17-Jan-63	PPCo Project Engineering Branch	19,000	Co-60	150,000
T27	30-Nov-62	PPCo Test Area North	Unknown	Unknown	24,000
T30	31-May-63	No data	Unknown	Co-60, Co-68, Fe-59	20,000
T26	28-May-62	GE-NMPO	7,000	Unknown	10,000
T29	11-Mar-63	Unknown	510	Co-60, Co-68, Fe-59, U-235	6,125
T26	06-Jul-62	GE-NMPO	0.0034	Unknown	4,000
T30	15-May-63	No data	250	Co-60, Co-68, Fe-59	3,000
T29	14-Mar-63	Unknown	167.4	Co-60, Co-68, Fe-59, U-235	2,009
T35	23-Oct-64	Metallurgy and Hot Cells	220	Unknown	2,000
T19	19-Jul-60	Engineered Test Reactor Operations	610	Unknown	1,840
T20	18-Jan-61	Central Facilities Laundry	0.6	Unknown	1,800
T25	29-Aug-61	Engineered Test Reactor Canal Waste	<285	Unknown	1,712
T25	18-Jan-62	Engineered Test Reactor Operations	249	Unknown	1,495
T28	18-Feb-63	Unknown	106	Co-60, Co-68, Fe-59, U-235, MFP	1,261
T19	20-Jul-60	Engineered Test Reactor Operations	376	Unknown	1,130
T19	19-Aug-60	Hot Shop Unit	300	Unknown	1,000
T25	25-Oct-61	G.E.	2,000	Unknown	1,000

Unfortunately, the radioisotopes contained in most of the packages at the time of disposal are shown as unknown on the disposal records. Without this information on the initial isotopics, the decay in the surface dose rates cannot be calculated adequately over time. For these packages, an estimate of the 2007 surface dose rate must be assumed conservatively to be the disposal dose rate. Therefore, the highest estimated surface dose rate at the initiation of grouting is 24,000 R/hr (the second entry in Table 2). Additionally, the surface dose rate must be assumed conservatively to be constant over the 1,000-year grout evaluation time frame because the decay over this time frame is unknown. The equation for the integrated dose is then:

$$\text{Integrated Dose (R)} = \text{Disposed of Surface Dose Rate (R/hr)} \times 1{,}000 \text{ y} \times 8{,}760 \text{ hr/y} \tag{1}$$

A rough idea of the amount of conservatism introduced by assuming no decay from time of disposal through the 1,000 year evaluation timeframe can be provided by using an integration of the half life decay curve for several isotopes that have a range of half lives. If only Co-60 (5.27 y half life) comprised the unknown isotopes, the conservative approach (assuming a 1981 disposal) would produce an integrated dose about 4,000 times higher than the actual dose. If the isotopes had longer half lives, for example pure Cs-137 (30.1 y half life) or Ni-63 (100.1 y half life), the integrated doses would be conservative by factors of about 42 and eight, respectively.

Based on the conservative assumptions for integrated dose, the potential for radiation-induced grout damage depends on the identified damage limits and the disposed of surface dose rate. Uncertainties in the damage limits suggest the need to examine the effects of three potential limit bounds. The first two bounds represent the consensus (Kaplan 1983, Alexander 1967, Sommers 1969) from the literature reviewed; the third bound was identified in one study (Soo and Milian 2001), but represents a much lower level of radiation exposure, so is included for completeness. The first limit to be examined is 10^{10} R. Much of the literature indicates no damage to concrete below this limit. The second limit is 2×10^{11} R, which if approached could result in reductions in compressive strength between 25 and 60 %. The third limit is 10^{7} R, which could result in reductions in compressive strength between 15 and 25% for low irradiation rates typical of waste. How this limit integrates with the 10^{10} R limit is unclear because there is insufficient data to adequately relate the two. A brief description follows of the influence of using each of these damage limits.

Disposed of surface dose rates that will cause the integrated dose to exceed 10^{10} R can be determined by inserting the limit on the left hand side of Equation (1) and solving. The disposed of surface dose rate that will result in 10^{10} R is 1,141 R/hr. Comparing this value with the results in Table 2 shows that 14 buried packages exceed this surface dose rate. Six of these packages have Co-60 as a major radionuclide, indicating there should be sufficient decay that the dose rate limit should not be exceeded. This leaves eight packages disposed of in the pits and trenches that would probably exceed the 10^{10} R integrated dose limit and therefore have the potential to cause reduced compressive strength.

The potential reductions in compressive strength that could be caused by these eight packages can be examined using the integrated dose value of 2×10^{11} R discussed previously. Inserting 2×10^{11} R into Equation (1) and solving yields a disposed of surface dose rate of 22,831 R/hr. Comparing this value with the results in Table 2 shows that there are two buried packages that exceed this limit. The dose rate of 150,000 R/hr had Co-60 as a primary isotope and, when decay is considered, should not exceed the calculated surface dose rate limit. The dose rate of 24,000 R/hr is very close to the value of 22,831 R/hr and is expected to cause similar amounts of compressive strength degradation. Based on these results, these eight packages are expected to cause a reduction in compressive strength between 25 and 60% for the surrounding grout. Table 3 lists these packages buried in the pits and trenches.

The effect of the lowest limit on integrated dose can be assessed using 10^{7} R for the left hand term in Equation (1). The calculated limiting dose rate for this value is 1.14 R/hr. Examining results presented in EDF-3543 for the full spectrum of pit and trench disposals shows there are about 849 disposals that exceed a surface dose rate of 1.14 R/hr. About 186 of these disposals have Co-60 identified as an isotope and it is estimated that 184 of these will have decayed to less than 1 R/hr. Removing these from the total, leaves 661 packages probably exceeding the calculated surface dose rate limit. Eight of these, identified in Table 3, exceed the integrated dose of 10^{10} R, leaving 653 packages that could cause limited reductions in compressive strength. At low irradiation rates typical of waste, the results of Soo and Milian (2001) indicate reductions in compressive strength of 15 to 25% at integrated doses near 10^{7} R but provide no information on changes in compressive strength as 10^{10} R is approached. To allow an integrated picture of compressive strength, assume that the compressive strength of surrounding grout drops by 25% when the integrated dose exceeds 10^{7} R, and 60% when the integrated dose exceeds 10^{10} R. This conservative approach would indicate 653 packages disposed of in the pits and trenches would cause a 25% reduction in the compressive strength of the surrounding grout and the eight packages listed in Table 3 would cause a 60% reduction.

Table 3. Eight disposals buried in the Subsurface Disposal Area pits and trenches that have the potential to result in degradation of concrete compressive strength based on 10^{10} R and 2×10^{11} R limits.

Disposal Location	Disposal Date	Originating Organization	Activity (Ci)	Isotopes	Surface Dose Rate (R/hr) at Disposal
T27	30-Nov-62	PPCo TAN	Unknown	Unknown	24,000
T26	28-May-62	GE-NMPO	7,000	Unknown	10,000
T26	06-Jul-62	GE-NMPO	0.0034	Unknown	4,000
T35	23-Oct-64	Metallurgy and Hot Cells	220	Unknown	2,000
T19	19-Jul-60	Engineering Test Reactor Operations	610	Unknown	1,840
T20	18-Jan-61	Central Facilities Laundry	0.6	Unknown	1,800
T25	29-Aug-61	Engineered Test Reactor Canal Waste	<285	Unknown	1,712
T25	18-Jan-62	Engineered Test Reactor Operations	249	Unknown	1,495

In assessing the implications of these conservative results, recognize that damage to the grout will be highly localized because cement is a good radiation shielding material and much of the radiation will be absorbed very close to the radiation source. Reductions in compressive strength and other mechanical properties therefore will occur only at locations very close to the radiation source. As a result, the structural integrity of the waste-grout mixture will depend strongly on how grouting is carried out (local formation of columns versus global formation of contiguous columns) and the design of the cap and the design (location and size) of supporting grout columns or groups of contiguous columns.

The implications of reductions in compressive strength can be determined by examining the results presented in Section 4.3.1. Examination of compressive strength for mixtures of grout with soil and simulated waste indicates that compressive strength would not be reduced below the NRC limit of 60 psi for the following grout scenarios even if there were a 60% reduction in compressive strength, which is the maximum reduction attributed to irradiation:

- Grout with soil loadings up to and including 50 wt% for GMENT-12, TECT HG, U.S. Grout, and Saltstone
- Grout with organic sludge loadings up to and including 9 wt% for GMENT-12, TECT HG, U.S. Grout, and Saltstone
- Grout with nitrate salt loadings up to and including 25 wt% for GMENT-12, TECT HG, and U.S. Grout
- Grout with thermal desorption-treated organic waste loadings up to and including 30 wt% for GMENT-12, TECT HG, and U.S. Grout (Saltstone not tested)

- Grout with soil loadings from 29 to 43 wt% for TECT 1 and Portland Type I cement
- Grout with soil or organic waste at about 40 wt% for TECT 1.

The relative importance of compressive strength compared to other performance parameters for grout will depend on the requirements (e.g., contaminant immobilization or structural support) and location (e.g., type of waste) for the grout.

4.2.6 Biodegradation

Concrete has historically been used to solidify and stabilize low-level waste because of its apparent structural strength and integrity. However, mechanical strength is not necessarily strongly correlated to concrete's ability to resist attack by chemical and physical agents. The environment in which concrete is placed is an important factor in concrete's long-term durability. The mechanisms of degradation that concrete would likely encounter in the environment include: sulfate and chloride attack, alkali-aggregate reactions, leaching by water, freeze-thaw cycling, salt crystallization, attack by low-level waste, and microbiological attack (Clifton and Knab 1989). Degradation of cement-based grouts can result from attack in situ by microorganisms (i.e., microbial-induced corrosion [MIC]). The MIC is corrosion resulting from the presence or activities of microorganisms that may include bacteria, fungi, or algae (Knight, Cheeseman, and Rogers 2002; Rogers et al. 2003). The basic causes of MIC include products of metabolism, such as the formation of acids, and metabolism of the substrate, biodegradation, or a combination of these mechanisms, involving more than one microorganism genus. Deterioration of concrete from both of these mechanisms has been observed

The MIC of concrete is a function of the macroenvironmental conditions, the changing microenvironmental conditions, and the bioavailability of nutrients and energy. Macroenvironmental conditions would include parameters such as mean temperature, mean precipitation, organic content of soil surrounding the concrete, geology, hydrology, biodiversity, and succession. Microenvironmental conditions would include parameters such as localized bioavailability of nutrients, localized population dynamics, including species diversity, interactions between species, and population fluctuations with respect to cycling of minerals and nutrients (e.g., autotroph → heterotroph → decomposer → autotroph) (Rogers, Hamilton, and McConnell 1993).

Typically, a habitat that supports microbial growth is populated by a community of bacteria that effectively cycles hydrogen, oxygen, carbon, and other essential elements and compounds. As environmental conditions fluctuate, populations of species also fluctuate. Municipal landfills are one area where microbial degradation of concrete has been observed. The presence of microbial activity in municipal landfills can in part cause the production of organic acids that are the cause for contaminant migration and concrete degradation. The same thing can occur in low level radioactive waste disposal sites, although in most cases the microbial activity is much lower (McGahan 1987).

In municipal landfills, organic matter from human waste provides needed sources of carbon and nutrients. In low-level radioactive waste disposal sites, the organic matter can come from waste such as clothing, plastics, paper, rubber, solvents, oils, ion exchanges resins, liquid scintillation cocktails, and solidification agents. The breakdown of these materials by microbial activity can lead to the formation of organic acids and sulfides that cause concrete degradation. However, limitations on the amount of moisture and types of organic material present in the waste tends to result in lower microbial activities in low-level waste sites compared to municipal waste landfills. Thus degradation rates for concrete are also expected to be lower (McGahan 1987).

The three major groups of organisms that are the primary contributors to corrosion or biodegradation of concrete are fungi, algae, and bacteria. Fungi are heterotrophic decomposers that obtain nutrients from nonliving organic matter (saprophyte) or living organic matter (parasite) (Wong 2003). Fungi secrete enzymes that dissolve this organic matter so that the nutrients can be transported across the cell membrane. Although fungi are found in the soil, a medium that contains no organic matter would not be degraded or an environment that is very limited in organic matter would not sustain a significant population. However, enzymes secreted by fungi to dissolve organic matter in proximity to a concrete structure would induce some degradation of the concrete. Algae are autotropic and obtain energy from photosynthesis, a process that converts light energy into chemical energy. In the presence of sunlight, algae convert carbon dioxide and water to organic matter. Algae also obtain nutrients and minerals from the environment. Fungi are decomposers and algae are primary producers. In a soil environment, such as the SDA, substantial growth of algae or fungi would be limited to primarily the upper soil horizons. Since the waste is primarily below these regions (the waste is generally 0.9 to 1.8 m [3 to 6 ft] below the ground surface, excluding the depth of the cap that is expected to be placed over the SDA) substantial degradation of jet grouted Portland-cement-based grout by fungi and algae will not occur.

Microbial-induced grout corrosion from sulfur-oxidizing bacteria living under aerobic conditions has also been observed (Gollop and Taylor 1996, Rogers et al. 1993, Rogers et al. 1995). Some bacteria are also autotrophs and obtain their energy by chemosynthesis. These primary producers obtain energy from oxidation-reduction reactions of inorganic matter. *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* are two bacteria that are acidophiles (Suzuki, Chan, and Takeuchi 1992) and obtain energy during the oxidation of inorganic sulfur or reduced sulfur (Kuenen, Robertson, and Tuovinen 1992). *T. ferrooxidans* can also oxidize inorganic iron (Suzuki, Chan, and Takeuchi 1992). The optimum conditions for sulphide oxidation to sulphuric acid and growth of *T. ferrooxidans* are the same: greater than 1% mole fraction oxygen, 30°C (80°F) (temperature range 5 to 55°C [41 to 131°F]), and a pH of 3.2 (pH range 1.5 to 5.0) (Rogers et al. 1995). Sulfuric acid attack on concrete is well documented in the literature for sewage pipes constructed of concrete. In sewage pipes, hydrogen sulfide is produced by aerobic decomposition of sulfur-containing amino acids and anaerobic desulfurication by sulfate-reducing bacteria such as *Desulfovibrio desulfuricans*. Sulfate-reducing bacteria are obligate anaerobes and grow well in media with pH values between 5.5 and 9 (optimum pH about 7.2), and temperatures between 20 and 50°C (68 and 122°F), although they can grow at higher and lower temperatures (Rogers, Hamilton, and McConnell 1993).

The SDA is generally an aerobic environment (Rightmire and Lewis 1987); therefore, it would support aerobic decomposing of sulfur-containing amino acids and other organic matter. Aerobic conditions also favor oxidation of reduced sulfur to sulfate by Thiobacilli. The pH of soil in the SDA is slightly alkaline, generally a pH of about 8 (Mincher et al. 2003), which is within or near the range of conditions for growth of some sulphuric acid producing microorganisms. The temperature of the soil varies with the season and with depth. The temperature of the soil surrounding the waste will generally range from 7 to 15°C (44.6 to 59°F), which is below the optimum temperature for the microorganisms discussed, but within the range of viability for a slower rate of growth. This suggests the degradation rate of cement-based grouts in the SDA would be slower than that observed in the cited references.

The three primary forms of internal sulfate attack on concrete (Scrivener and Skalny 2002) are:

- Contamination of the aggregates by sulfates
- Over sulfation of the cement
- Delayed ettringite formation.

The literature search indicates that one of the most aggressive mechanisms for degradation of concrete is sulfate attack. Severe concrete degradation by Thiobacilli from biogenic sulfuric acid corrosion has been demonstrated ex situ (Sand 1987). In situ environments potentially provide nutrients, temperature, and moisture and humidity that promote growth and vitality of the genus Thiobacillus, an acidophilic microbe typically indigenous in the soil, especially in environments containing sulphur compounds. Thiobacillus oxidizes sulfides to sulphuric acid. The sulfate anion migrates into the concrete and reacts with constituents of the concrete. Two identified products of sulfate attack on concrete are the formation of gypsum (sulfate reacting with calcium hydroxide) and the formation of ettringite (sulfate reacting with hydrated calcium aluminate). Both products of these reactions are compounds that are larger than the initial constituents, causing cracking of the concrete matrix. Hydrogen ions also react with components of concrete to cause decomposition.

The mechanisms of concrete degradation have been postulated, but rates of decomposition are highly variable because conditions are highly variable. Even at a particular location, environmental conditions vary seasonally. Perhaps the largest amount of field data for actual data on concrete degradation is concrete sewer structures. In these cases, the concrete degradation rates are as high as 4.3 to 4.7 cm/yr (1.7 to 1.9 in./yr). However, the conditions in a sewer system favor bacterial growth—near saturated water content and an abundance of nutrients. Biocorrosion rates elsewhere are generally slower, ranging from 1 to 5 mm/yr (0.04 to 0.2 in./yr) (Mori et al. 1991), but studies have reported rates as high as 1 cm/yr (0.4 in./yr) (Knight, Cheeseman, and Rogers 2002). In most of these studies, a nutrient solution is used to increase biological growth on the concrete surface. Table 4 lists some of the compositions used in these studies. Compared to the expected composition of the groundwater and soil in the SDA at the INL Site (Tables 5 and 6), the solutions used in the reported studies contained more nitrogen (ammonia), phosphorous, and potassium than the groundwater and had a much lower pH, favoring acid-producing bacteria. In addition, the studies were also conducted at higher temperatures (25°C [77°F]) than would be expected in the subsurface (7 to 10°C [44.6 to 50°F]). In situ degradation at the SDA would likely occur, but at slower rates than those reported in the literature cited.

In addition to the variability of the environment, the presence and concentration of microbes and electron donors, the variability in concrete mixes, and the variability in waste further compound the ability to quantify corrosion and degradation. Although the literature does address MIC, the majority of the literature identifies only qualitative relationships between properties of the medium and the extent of biological responses with respect to corrosion rates. The current state of the art for MIC does not address corrosion rates because, to date, experiments lack reproducibility, fundamental mechanisms of MIC are not thoroughly understood or are not thoroughly defined, and there are no direct methods to measure MIC corrosion rates. The degree of MIC depends on the number of microorganisms and the species of microorganism, assuming that nutrients and energy are not limiting. Metabolic activity of organisms produces by-products that chemically change the environment or microenvironment. In the case of Thiobacilli, as the population grows, the acidity of the microenvironment becomes more acidic, resulting in an increasing favorable environment for this microorganism. As the population increases with respect to time, or as the population increases with successive population cycles, corrosion rates will also increase.

Table 4. Solution used to promote biological growth on concrete.

Constituent	Grams per Liter of Nano Pure Water a	b
Calcium	0.036	0.078
Magnesium	0.056	0.039
Sulfide		1.5
Iron	0.0037	
Phosphate	2.13	0.814
Chloride	0.064	0.137
Sulfate	0.62	0.52
Potassium	2.4	1.18
Ammonia	0.115	0.136
pH	1.9 (pH units)	1.6 (pH units)

a. Knight, Cheeseman, and Rogers (2002).
b. Idachaba, Nyavor, and Egiebor (2003).

Table 5. Subsurface Disposal Area water simulant recipes for in situ grouting and in situ thermal desorption leach testing.

Constituent	Vadose Zone Water[a] (grams per liter of nano pure water)
Calcium	0.88
Magnesium	0.36
Sodium	0.16
Silica	0.46
Iron (total)	0.060
Chloride	0.22
Sulfate	0.46
Potassium	0.038
Alkalinity (as calcium carbonate)	3.3
pH	8.0 (pH units)

a. Adapted from Yancey et al. (2003).

Table 6. Analysis of soil from Idaho National Laboratory Site.[a]

Data	Value
Resistivity: Wenner array ohm-cm	10,000
Resistivity: Miller box ohm-cm (saturated)	2,750 to 4,500
Moisture content (%)	3.45 to 13.7
Soil pH (in 0.01M $CaCl_2$)	8.1 to 8.3
Acidity (meq/100 g)	3.4 to 16.2
Soluble Ions (meq/100 g)	
Calcium (Ca^{-2})	0.11 to 0.25
Magnesium (Mg^{+2})	0.07 to 0.26
Potassium (K^{+})	0.004 to 0.01
Sodium (Na^{+})	0.028 to 0.05
Carbonate (CO_3^{-2})	ND
Bicarbonate (HCO_3^{-1})	0.10 to 0.29
Sulfate (SO_4^{-2})	0.02 to 0.05
Sulfide (S^{-2})	ND
Chloride (Cl^{-})	0.006 to 0.02
Exchangeable Cations (meq/100 g)	
Calcium (Ca^{2+})	14.1 to 44.1
Magnesium (Mg^{2+})	3.94 to 11.9
Potassium (K^{+})	0.54 to 1.19
Sodium (Na^{+})	0.09 to 0.22
Cation Exchange Capacity (meq/100 g)	
Exchangeable bases	19.05 to 57.41
Exchangeable acidity	3.4 to 16.2
Cation exchange capacity	27.1 to 50.4

a. Adapted from Adler Flitton et al.(2004).

4.2.7 Carbonation

Carbonation of cement can alter the performance by reducing the pH, changing the mineralogy, and altering the physical properties of the cement. Carbonation occurs when carbon dioxide (gas phase) or bicarbonate (liquid phase) diffuse into cement and react with the existing mineralogy (Smith and Walton 1991; Steffens, Dinkler, and Ahrens 2002; Lange, Hills, and Poole 1996; Anstice, Page, and Page 2005). Carbonation involves a complex set of reactions that depend partially on the specific formulation of the cement, the contaminants present, and the concentration of carbon dioxide present, but the major reaction for carbonation can be stated in Equation (2) as follows:

$$CO_2 + Ca(OH)_2 \xrightarrow{H_2O} CaCO_3 + H_2O \quad (2)$$

While carbonation is generally a slow process, the rate depends on the concentration of carbon dioxide (or bicarbonate) and the degree of hydration of the cement (Smith and Walton 1991; Steffens, Dinkler, and Ahrens 2002). Although water is required for carbon dioxide to react with cement, the diffusion of carbon dioxide is significantly slower through wetted cement than through dry cement (Steffens, Dinkler, and Ahrens 2002).

Carbonation can both improve and impair the performance of cement. Carbonation can increase the compressive strength (Lange, Hills, and Poole 1996) and density of cement (Anstice, Page, and Page 2005). Carbonation can both decrease the porosity (desired) and increase the number of connected pores (not desired) within cement (Anstice, Page, and Page 2005). As carbon dioxide penetrates cement, it reacts with minerals present to form calcite. Then, depending on the specific contaminant, this may result in enhanced immobilization of contaminants (Lange, Hills, and Poole 1996; Smith and Walton 1991; Curti 1999). However, the formation of calcite within the existing cement structure can also generate microcracks and change the solubility of the cement matrix. In addition, the stability of a protective passive film that forms on carbon steel embedded in cement depends on the high pH (i.e., greater than 12) of the cement. This film can be damaged by carbon dioxide diffusing into the cement, which eventually lowers the pH, destabilizes the passive protective film, and allows corrosion of the carbon steel.

Carbonation in cement can be modeled as a front of pH less than or equal to 9, slowly penetrating inward from the surface of the cement. Two models developed by Steffens, Dinkler, and Ahrens (2002) and Smith and Walton (1991) provide the basis for estimating the carbonation rate of cement in the SDA. This estimate focuses on the carbonation rate due to diffusion of carbon dioxide into the cement. Cement used to stabilize waste would be placed in the vadose (unsaturated) zone and measurements in the SDA have confirmed the presence of carbon dioxide in the subsurface (INEEL 2000). The conditions and assumptions of the two models do not exactly match each other or the conditions at the SDA (see Table 7), but they are close enough to make a reasonable estimate of the rate of carbonation at the SDA.

Table 7. Comparison of model conditions and assumptions to expected Subsurface Disposal Area conditions.

Parameter	Steffens, Dinkler, and Ahrens (2002) Model	Smith and Walton (1991) Model	Subsurface Disposal Area Conditions
Carbon dioxide concentration	5.56×10^{-1} atm	3.12×10^{-3} atm	1.26×10^{-1} atm[b]
Water/cement ratio	0.7	0.42	Unknown but expected to be in that range
Carbon dioxide diffusion coefficient	6.64×10^{-4} cm_2/s	5×10^{-7} cm_2/s[a]	Unknown for soil in Subsurface Disposal Area but expected to be in that range; for grouted waste, it is unknown but is expected to be lower than for soil
Hydration	Cement hydrated, not directly exposed to rain	Cement hydrated, soil partially saturated	Unsaturated soil

a. Diffusion coefficient × tortuosity.
b. Maximum recorded value.

The estimate of the carbonation rate for the SDA was interpolated from the carbonation rates given in the two models (see Table 8) based on the carbon dioxide concentration in the soil at the SDA compared to the concentrations of carbon dioxide used in the models.

Table 8. Carbon dioxide concentrations and carbonation rates from models.

Model	Carbon Dioxide Concentration (P_{CO2})	Carbonation Rate
Steffens, Dinkler, and Ahrens (2002)	5.56×10^{-1} atm	2.60×10^{-1} mm/yr
Smith and Walton (1991)	3.12×10^{-3} atm	2.00×10^{-2} mm/yr

The following were assumed in estimating the carbonation rate of cement in the SDA:

- Carbonation rate is linear with respect to CO_2 partial pressure
- System is unsaturated
- Water/cement ratios in the cement grouted waste in the SDA would be similar to those used in the models
- The diffusion rate of carbon dioxide through the cement grouted waste in the SDA would be on the order of those used in the models.

$$\text{rate} = mP_{CO2} + b$$

from Table 8:

rate 1 = 2.00×10^{-2} mm/yr $P_{CO2}1 = 3.12 \times 10^{-3}$ atm

rate 2 = 2.60×10^{-1} mm/yr $P_{CO2}2 = 5.56 \times 10^{-1}$ atm

$$m = \frac{\text{rate}\,2 - \text{rate}\,1}{P_{CO2}2 - P_{CO2}1} = 4.34 \times 10^{-1} \text{ mm/yr/atm}$$

$$b = 1.86 \times 10^{-2} \text{ mm/yr}$$

$$\text{rate} = 4.34 \times 10^{-1} * P_{CO2} + 1.86 \times 10^{-2}$$

$$\text{for } P_{CO2} = 1.26 \times 10^{-1} \text{ atm}$$

$$\text{rate} = 7.34 \times 10^{-2} \text{ mm/yr}$$

In 1,000 years the carbonation front in the SDA is estimated to move 73.4 mm (2.9 in.) into the cemented waste.

4.2.8 Groundwater Leaching

Groundwater leaching can degrade performance of cement over time. The pH of groundwater at the SDA is 7 to 8 (INEEL 2000; Liszewski et al. 1998; Bartholomay et al. 1995; Orr and Cecil 1991; Mundorff, Crosthwaite, and Kilburn 1964; Wood and Low 1986; Del Debbio 1991), while the pH of cement is greater than or equal to 12. When groundwater contacts cement, it can dissolve portions of the cement, leading to a decrease in pH and a change in mineralogy of the cement (Alcorn, Coons, and

Gardner 1990; Clifton and Knab 1989). The NRC has developed a model to predict migration because of groundwater leaching of a 10.5 pH front into concrete (Cliffton and Knab 1989).

The model assumes the following:

- Initial pH of concrete = 12.5
- No freeze-thaw cycling
- Permeability of concrete = soil permeability
- Initial concrete monolith is 20 m (65.6 ft) in radius
- Groundwater flux = 1×10^{-10} m/s.

The model predicts that the 10.5 pH front will move toward the center of the concrete mass at a rate of 1 m (13.1 ft) per 1.5×10^{5} years or 6.67×10^{-3} mm/yr.

The conditions for in situ grouting in the SDA are expected to be very similar to those used for the model above. Table 9 shows the composition and density of several test samples that simulate SDA grouting conditions. Density of cement in the test samples is greater than overall density of cement in concrete assumed for the NRC model of 1.85×10^{-1} g/cm^3. Density of soil in the SDA is approximately 1.6 g/cm^3 (0.06 lb/in.^{3}), while density of the cement is approximately 1.8 to 2.2 g/cm^3 (0.07 to 0.08 lb/in.^{3}). The greater density of cement in the sample indicates more cement in the sample and therefore more resistance to pH shift. Like the model, the initial pH of the concrete is expected to be greater than or equal to 12.5; the grouted region will be below the frost line and therefore will avoid freeze and thaw cycles. In recent laboratory tests (Matthern et al. 2005), the permeability of the concrete (i.e., Portland-cement-based grout plus soil) was less than that of the soil. Waste that could be grouted in the SDA is in the vadose zone, so groundwater flow would be intermittent rather than constant as in the model. The pH of groundwater used in the model is not known, but the pH of groundwater at the SDA is approximately 8.

Table 9. Composition and density of several Portland cement formulations under consideration.

Mix	Soil (wt%)	Water (wt%)	Cement (wt%)	Slag (wt%)	Fly Ash (wt%)	Thiosulfate (wt%)	Density of Concrete (g/cm^3)	Mass of 100 cm^3 of Concrete (g)	Overall Density of Cement in Concrete (g/cm^3)
Cement	46.8	8.7	44.5	0	0	0	2.09	209	9.30E-01
Cement + slag	53.9	7.5	19.4	19.2	0	0	2.07	207	4.02E-01
Cement + fly ash	43.4	10	23.2	0	23.2	0	2.08	208	4.83E-01
Cement + fly ash + thiosulfate	42.3	9.7	24.4	0	23.4	0.1	2.01	201	4.90E-01
Cement + slag + thiosulfate	46.6	10	22	21.7	0	0.1	2.01	201	4.42E-01

The void fraction of the soil is approximately 30 vol% and the void fraction in the containerized waste is approximately 50 vol%. The samples prepared in Table 9 had a nominal 50 wt% soil loading in grout; this is approximately the grout content for soil with 30 vol% void space. The Portland cement formulation for a soil loading of 70 wt% is shown in Table 10.

Table 10. Portland cement formulation for a soil loading of 70 wt%.

Mix	Soil (wt%)	Water (wt%)	Cement (wt%)	Slag (wt%)	Fly Ash (wt%)	Thiosulfate (wt%)	Density of Concrete (g/cm^3)	Mass of 100 cm^3 of Concrete (g)	Overall Density of Cement in Concrete (g/cm^3)
Cement	70	4.91	25.09	0	0	0	2.09	209	5.24E-01
Cement + slag	70	4.88	12.62	12.49	0	0	2.07	207	2.61E-01
Cement + fly ash	70	5.30	12.30	0.00	12.30	0.00	2.08	208	2.56E-01
Cement + fly ash + thiosulfate	70	5.04	12.69	0.00	12.17	0.05	2.01	201	2.55E-01
Cement + slag + thiosulfate	70	5.62	12.36	12.19	0.00	0.06	2.01	201	2.48E-01

Assuming the density of the concrete remains constant, overall density of the cement in the concrete is greater than 1.85×10^{-1} g/cm^3. Since density (content) of the cement in the concrete (or grouted region) relates directly to amount of material to leach, grouted regions in the SDA should be more resistant to pH shift than predicted by the model. Thus the rate of progression of the 10.5 pH front in grout material in the SDA should be less than 6.67×10^{-3} mm/yr.

4.2.9 Physical Properties

The physical properties of cementitious grouts are important to all three potential applications of grout: immobilization, structural support, and retrieval. Jet grouting is the probable method of placement for all three potential applications of grout in the SDA. A brief description of the physical properties of cementitious grouts that could be important to jet grouting is provided to aid in understanding and analyzing successful jet grouting. The most important physical properties are primarily density and viscosity. Thermal properties are also included because heat capacity and thermal conductivity will influence solidification time and the general behavior of the grout in the vicinity of materials, such as metal forms, that can have different thermal properties than the majority of the waste. This information is particularly useful if calculations on the behavior of the grout are necessary for understanding behavior during or shortly after jet grouting.

4.2.9.1 Density and Viscosity. The density of the placed grout will depend greatly on the quantity and density of soil and/or waste encapsulated in the grout paste. Likewise, viscosity depends greatly on the quantity of excess water, the degree of cure, particle sizes of all components, and amendments that may be added to control set time. EDF-5333 reports typical densities and viscosities for grout paste without incorporation of matrix components that are summarized in Table 11 for several grout types.

4.2.9.2 Specific Heat. As with other grout properties, the bulk specific heat of the placed grout will be a function of the paste and the aggregate materials incorporated in the grout. The literature search did not reveal specific heat data for the cement-based proprietary grouts discussed in this report. However, Perry 1937 lists specific heat data for a variety of inorganic mineral materials, indicating that a value of approximately 0.2 cal/g-C would be reasonable for cement-based grouts. Table 12 presents specific heat values for a variety of inorganic mineral materials.

Table 11. Density and viscosity of various cement-based grouts.

Company	Trade Name	Viscosity (Marsh Funnel Time)	Density (g/cc)
Ash Grove Cement	Type I-II, V, or H	50 to 200	2.2
Carter Tech	TECT HG	113	2.2
U.S. Grout	Microfine	58	1.7
Tech Venture	GMENT	56	2.1
Generic	Saltstone	110	1.6

Table 12. Specific heat values for inorganic mineral materials.

Material	Specific Heat (cal/g-C)
Alumina	0.2
Asbestos	0.25
Brickwork	About 0.2
Cement, Portland Clinker	0.186
Clay	0.224
Concrete	0.219
Fireclay Brick	0.198
Gypsum	0.259
Limestone	0.217
Sand	0.191
Stone	About 0.2

4.2.9.3 Thermal Conductivity. The literature search did not reveal specific thermal conductivity data for the cement-based proprietary grouts discussed in this report. However, the Portland Cement Association (Kosmatka and Panarese 1994) presents a generalized correlation for cements that should be reasonably accurate. In this correlation, the primary factors influencing thermal conductivity are density and water content. Thermal conductivity of cement, as a function of density and moisture content, is presented in Figure 12.

Note that the bulk thermal conductivity of the placed grout will depend greatly on the thermal conductivity of the soil and waste form materials of the SDA. Certain impermeable materials in the SDA, including wood, paper, and fabric, have low thermal conductivity and may strongly influence the ability of the placed jet grout to dissipate the heat associated with the hydration reactions of the cement.

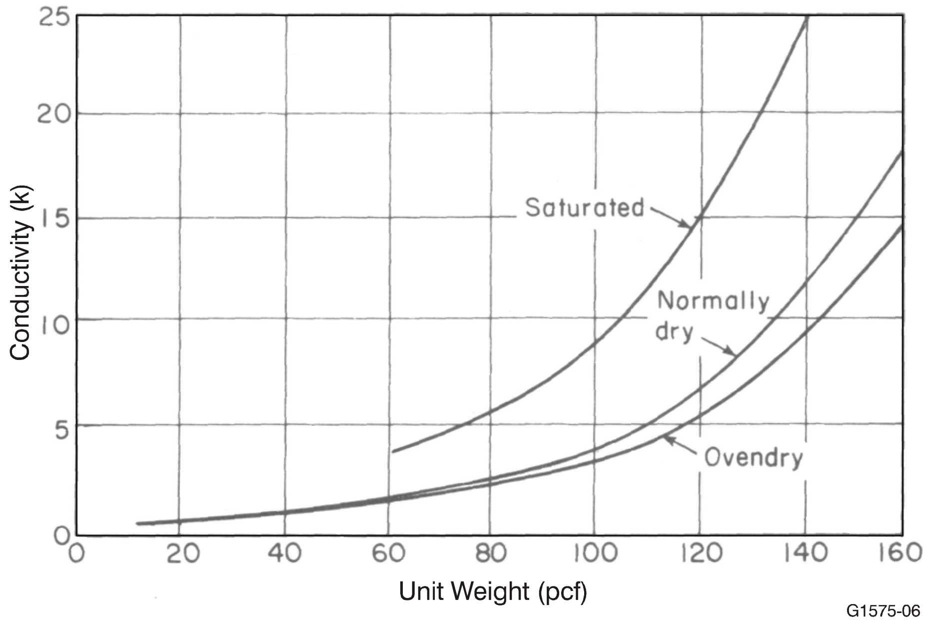

Figure 12. Approximate relationship between unit weight and thermal conductivity of concretes (Soo and Milian 2001).

4.2.9.4 Volume Contraction During Setting. The Portland Cement Association (Kosmatka and Panarese 1994) reports shrinkage rates of 0.1 to 0.6% with most values reported around 0.3%. Shrinkage is primarily a function of water content with increased shrinkage at a higher water content. Other factors influencing shrinkage include air entrainment, cement concentration, and aggregate coarseness. In the case of jet grouts in the SDA, higher water contents used to reduce viscosity may produce grouts that shrink more. Fracture of cement is more common when excess water is used.

4.3 Structural Support Properties with Subsurface Disposal Area Interferences

As mentioned earlier, Portland-cement-based grouts are candidates for providing physical support to a cap via columns and for placement as groups of contiguous columns for structural support, immobilization, or retrieval. Loading from the normal 1 to 2 m (3.3 to 6.6 ft) of overburden in the SDA is generally insufficient to make the need for support a major factor in the performance of surface material. However, support from grout columns or contiguous columns becomes increasingly important when a cap is constructed over the grouted waste to restrict moisture penetration. If the columns or monoliths do not provide adequate support for all areas of the cap, localized subsidence may cause ponding of water on the cap surface that could cause permeable pathways to develop through the cap to the grouted waste.

4.3.1 Compressive Strength

Understanding the unconfined compressive strength of jet-grouted soil or waste is important for calculating the future performance of the grouted areas because the grout columns or groups of contiguous columns are under stress from the overlying materials. Compressive strength values also provide a basis for assessing changes in the integrity of the grouted material, using results from tests on the effects of physical changes in, or chemical attack on, grouted material. Compressive strength is also an important consideration for retrieval; materials with very high compressive strengths may make retrieval more complicated.

Compressive strength results are provided for neat grouts and for grouts mixed with soil and waste. Information on compressive strength for neat grouts was gleaned from a variety of sources and includes both Portland-cement-based grouts and proprietary and commercial grouts. Results from compressive strength testing on grouts mixed with soil and waste were gleaned from recent and past testing at the INL Site (Matthern et al. 2005; Loomis et al. 2002), and from previous testing by Brookhaven National Laboratory (Milian et al. 1997).

4.3.1.1 Neat Grout Results. Results for neat grouts have been compiled to provide and compare the uncontaminated compressive strength of the different grouts. Table 13 provides data from two sets of tests performed at the INL Site. The results for GMENT-12 are in reasonable agreement, but the results for TECT HG and U.S. Grout are substantially different. Saltstone has only one set of results, which limits good comparisons.

Table 13. Compressive strength data for neat grout.

	Compressive Strength							
	GMENT-12		TECT HG		U.S. Grout		Saltstone	
Data Source	Average (psi)	95% CI[a] (psi)	Average (psi)	95% CI[a] (psi)	Average (psi)	95% CI[a] (psi)	Average (psi)	95% CI[a] (psi)
Yancey et al. (2005)	5,234	651	2,934	278	1,671	523		
Loomis et al. (2002)	4,395	2,760	7,339	729	8,820	709	1,383	110

a. 95% confidence interval.

4.3.1.2 Idaho National Laboratory Site-Sponsored Tests with Soil and Waste. Unconfined compressive strength of Portland-cement-based grouts has been tested for soil and waste loadings that cover the range of conditions expected in the SDA. Tests were conducted at the INL Site as part of preremedial design testing and predecessor testing to develop jet grouting formulations and techniques. Portland-cement-based grout compressive strength test results are presented for:

- Grout and soil mixtures
- Grout and simulated organic sludge mixtures
- Grout and nitrate salt mixtures
- Grout and mixtures of in situ thermally desorbed organic sludge.

Neat grout compressive strength is presented along with the soil and waste loading results for purposes of comparison.

The objective of the tests outlined above (Yancey et al. 2003, Loomis et al. 2002) is to determine whether materials similar to those that will be mixed with GMENT-12, TECT HG, and U.S. Grout during jet grouting at the SDA will have an adverse effect on the grout's compressive strength. Test results for cementitious grout test samples with no waste loading (i.e., neat grout) are presented with the other results to provide straightforward comparisons of the effects of soil and waste on compressive strength.

Compressive strength testing for the cementitious grouts used the "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens" (ASTM C39). Test results combine data from both Yancey et al. (2005) and Loomis et al. (2002) and are briefly described in the following subsections.

4.3.1.2.1 Grout-Soil Mixtures—The cementitious grouts and soil from the INL Site (sieved to 50 mesh) were mixed at loadings of 12, 25, 50, and 75 wt% and were poured into cylindrical samples and allowed to cure. Results from the compressive strength tests are presented in Table 14 and are presented graphically in Figure 13. The results show that increasing the amount of soil generally results in a decrease in the compressive strength. An exception is the 12 wt% soil loading for U.S. Grout where the compressive strength increased significantly above the neat grout value. Generally, GMENT and TECT HG were not capable of forming monoliths at 75 wt% soil loading, and consequently were assigned a value of zero for compressive strength.

Table 14. Compressive strength data for neat grout and grout-soil mixtures.

		Compressive Strength							
		GMENT-12		TECT HG		U.S. Grout		Saltstone	
Waste Type	Soil Loading (wt %)	Average(psi)	95% CI[a] (psi)	Average (psi)	95% CI[a] (psi)	Average (psi)	95% CI[a] (psi)	Average (psi)	95% CI[a] (psi)
Neat Grout	0	5,234	651	2,934	278	1,671	523	1,383	110
INL Site Soil	12	5,884	1,024	4,150	445	3,896	110	1,259	161
INL Site Soil	25	6,048	393	3,654	169	3,098	111	910	36
INL Site Soil	50	2,529	591	1,924	97	1,278	311	1,318	223
INL Site Soil	75	NSAM		NSAM		805	42.0	403	52

a. 95% confidence interval

INL = Idaho National Laboratory
NSAM = Not a stand-alone monolith (i.e., generally, could not form a stand-alone monolith for testing)

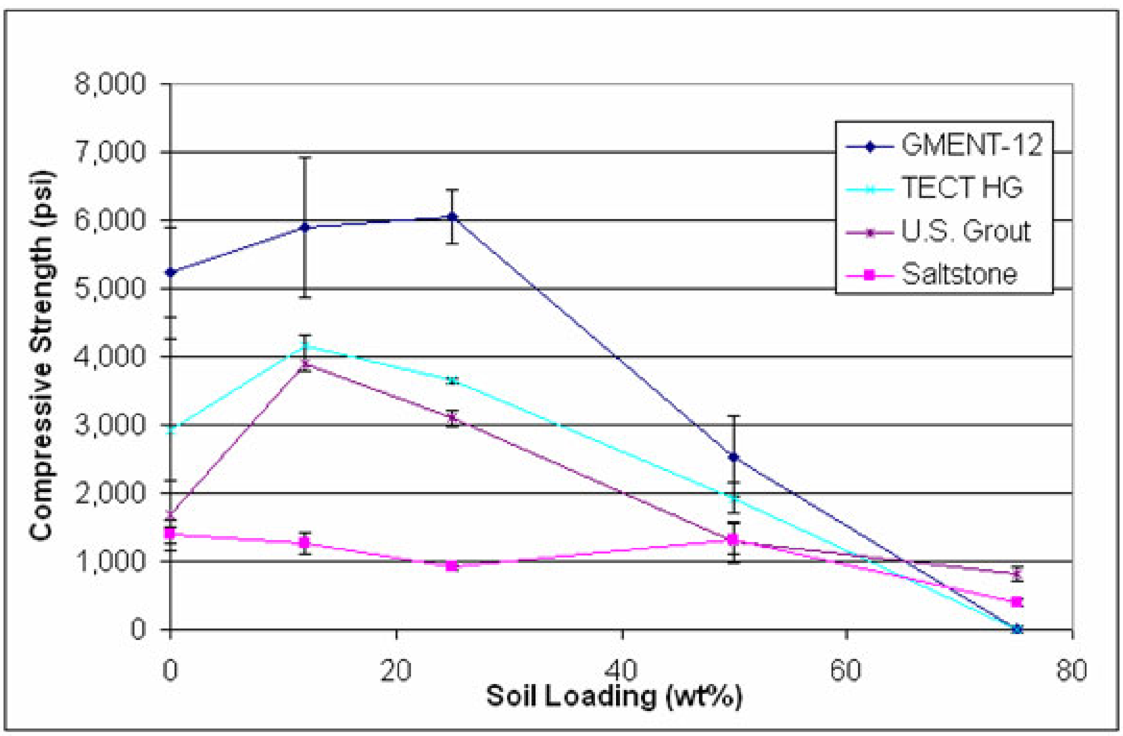

Figure 13. Compressive strength of cementitious grouts for neat grout and various soil loadings (Soo and Milian 2001).

All compressive strength values at soil loadings of 50 wt% or less are above the minimum 60 psi required by the NRC for hydraulic cements (NRC 1991). Soil loadings of 70% resulted in significantly degraded compressive strength for all grouts. Voids in the SDA soil are generally expected to be in the range of 50% or less.

4.3.1.2.2 Cementitious Grout/Simulated Organic Sludge Mixtures—Organic sludge in the TRU pits and trenches at the SDA represents a small percentage of the waste pit volume. However, there are zones where drums of organic sludge could make up the majority of the waste. A previous study (Loomis, Zdinak, and Bishop 1996) shows that jet grouting of highly organic materials can degrade grout curing and monolith stability. However, cementitious grouts tend to form cohesive monoliths when used to jet grout isolated drums of organic compounds (such as chlorinated hydrocarbons).

For the INL Site-sponsored tests, cementitious grouts were mixed with simulated Rocky Flats Plant organic waste. The simulated waste uses an organic formulation based on general knowledge of the typical composition of waste shipped to the INL Site from the Rocky Flats Plant. The simulated waste consists of trichloroethylene, tetrachloroethylene, carbon tetrachloride, and trichloroethane as volatile organics mixed with absorbers and Texaco Regal Motor Oil in the quantities shown in Table 15. This mixture of volatile organics, oil, and absorbers exhibits a grease-like consistency. Grouts were mixed with quantities of 3, 5, 7, 9, 12, 25, and 50 wt% simulated organic sludge. The resulting material was tested for compressive strength.

Table 15. Material proportions for the organic sludge mixture.

Ingredient	Quantity
Calcium silicate	4,120 g
Oil Dri	620 g
Carbon tetrachloride	2,680 mL
Tetrachloroethylene	740 mL
Trichloroethylene	740 mL
Trichloroethane	1,030 mL
Texaco Regal Oil, R&O 68	5,130 mL

Table 16 and Figure 14 present the results from the compressive strength tests. These results show that simulated organic sludge in quantities of about 9 wt% and greater significantly decrease the compressive strength of cementitious grouts. For loadings of 9 wt% organic waste loading or less, compressive strength values were above the minimum 60 psi required by the NRC (NRC 1991) to provide adequate support to overlying material.

Table 16. Compressive strength of cementitious grouts for neat grout and organic sludge loadings.

		Compressive Strength							
		GMENT-12		TECT HG		U.S. Grout		Saltstone	
Waste Type	Sludge Loading (wt %)	Average (psi)	95% CI[a] (psi)	Average (psi)	95% CI[a] (psi)	Average (psi)	95% CI[a] (psi)	Average (psi)	95% CI[a] (psi)
Neat Grout	0	5,234	651	2,934	278	1,671	523	1,306	110
Organic Sludge	3	7,349	1047	4,296	105	3,276	295	1,275	121
Organic Sludge	5	6,100	2,244	3,706	129	2,878	341	1,075	380
Organic Sludge	7	6,215	719	2,820	32	2,644	317	985	631
Organic Sludge	9	6,083	337	2,618	407	3,136	199	1,021	190
Organic Sludge	12	NSAM		2,347	93	NSAM		924	230
Organic Sludge	25	NSAM		204	0.0	NSAM		507	366
Organic Sludge	50	NSAM		7	5	NSAM		NSAM	

a. 95% confidence interval.

NSAM = Not a stand-alone monolith (i.e., generally, could not form a stand-alone monolith for testing)

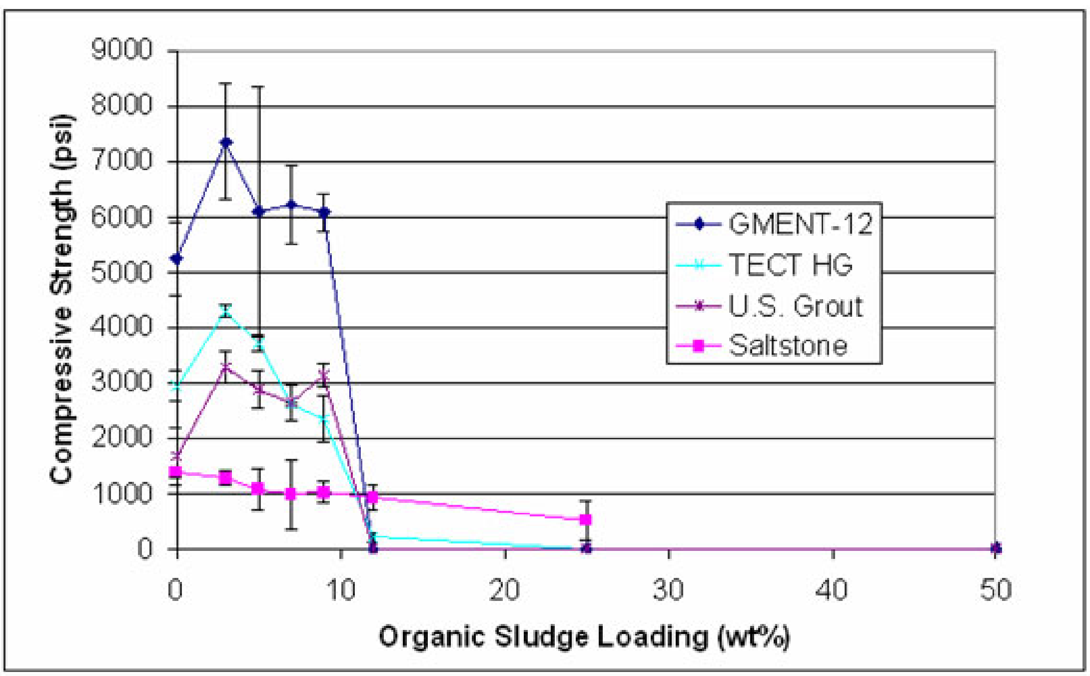

Figure 14. Compressive strength of cementitious grouts for neat grout and organic sludge loadings (Soo and Milian 2001).

4.3.1.2.3 Cementitious Grouts/Nitrate Salt Mixture—Granular nitrate salts (roughly 33% potassium nitrate and 67% sodium nitrate) were blended to represent evaporation pond salts from Rocky Flats Plant buried in TRU pits and trenches in the SDA. The candidate cementitious grouts were mixed with the nitrate salts at loadings of 12, 25, 50, and 75 wt%. Table 17 and Figure 15 present the data from the compressive strength testing.

Table 17. Compressive strength of cementitious grout for neat grout and nitrate salt loadings.

		Compressive Strength							
		GMENT-12		TECT HG		U.S. Grout		Saltstone	
Waste Type	Salt Loading (wt %)	Average (psi)	95% CI[a] (psi)	Average (psi)	95% CI[a] (psi)	Average (psi)	95% CI[a] (psi)	Average (psi)	95% CI[a] (psi)
Neat Grout	0	5,234	651	2,934	278	1,671	523	1,383	110
Nitrate Salt	12	3,171	3,520	3,239	191	4,802	1,079	700	196
Nitrate Salt	25	2,885	1,386	1,193	19	1,383	166	403	49
Nitrate Salt	50	3	1	NSAM		1,814	115	2	1
Nitrate Salt	75	104	19	NSAM		869	9	3	1

a. 95% confidence interval.

NSAM = Not a stand-alone monolith (i.e., generally, could not form a stand-alone monolith for testing)

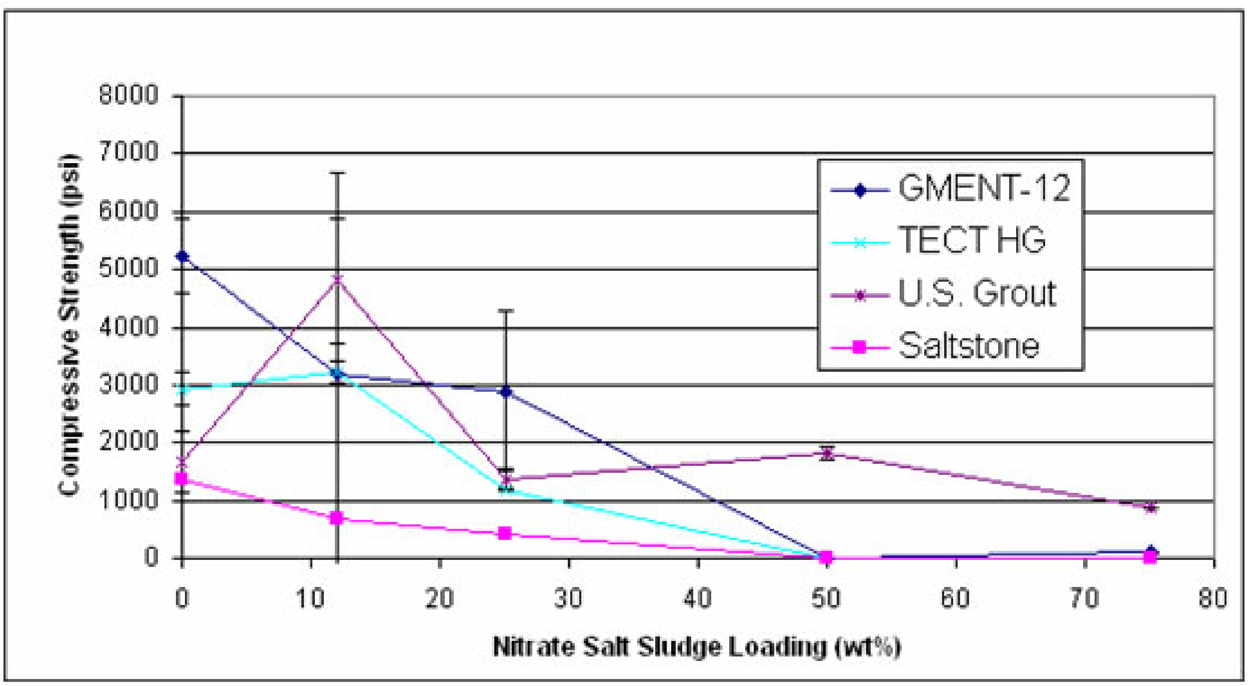

Figure 15. Compressive strength of cementitious grouts for neat grout and grout with nitrate salt loadings (Soo and Milian 2001).

Calculations are being conducted to assess the influence of compressive strength on the potential for subsidence. The nitrate salt loading decreased the compressive strength by about 30% (see Figure 15). This decrease was relatively constant over the range of nitrate salt concentrations tested. The compressive strength values for all nitrate salt waste loadings of 25 wt% or less were above the minimum 60 psi required by the NRC (NRC 1991) to provide adequate support to the overlying material.

4.3.1.2.4 Cementitious Grouts/Thermally Desorbed-Treated Organic Sludge Mixture—The thermal desorption process was expected to make the waste and cementitious grouts more compatible, thus increasing the maximum waste loading over that obtained for organic sludge. Portland-cement-based grouts were mixed with thermally desorbed-treated organic sludge at loadings of 5, 10, 15, 20, 30, and 50 wt%. Saltstone grout was not included in the thermally desorbed-treated sludge testing. Table 18 presents the compressive strength data for these tests. Figure 16 also graphically represents this data.

Table 18. Compressive strength of cementitious grouts for neat grout and thermally desorbed waste loadings.

		Compressive Strength							
		GMENT-12		TECT HG		U.S. Grout		Saltstone	
Waste Type	Sludge Loading (wt %)	Average(psi)	95% CI[a] (psi)	Average (psi)	95% CI[a] (psi)	Average (psi)	95% CI[a] (psi)	Average (psi)	95% CI[a] (psi)
Neat grout	0	5,234	651	2,934	278	1,671	523	NTP	
Thermally Desorbed-Treated Sludge	5	2,789	573	NTP		1,564	577	NTP	
Thermally Desorbed-Treated Sludge	10	2,749	573	1,857	553	1,631	309	NTP	
Thermally Desorbed-Treated Sludge	15	2,696	74	NTP		NTP		NTP	
Thermally Desorbed-Treated Sludge	20	2,629	545	2,146	473	2,116	335	NTP	
Thermally Desorbed-Treated Sludge	30	2,574	708	2,078	297	1,865	493	NTP	
Thermally Desorbed-Treated Sludge	50	1,398	358	881	251	853	374	NTP	

a. 95% confidence interval.

NTP = no testing performed.

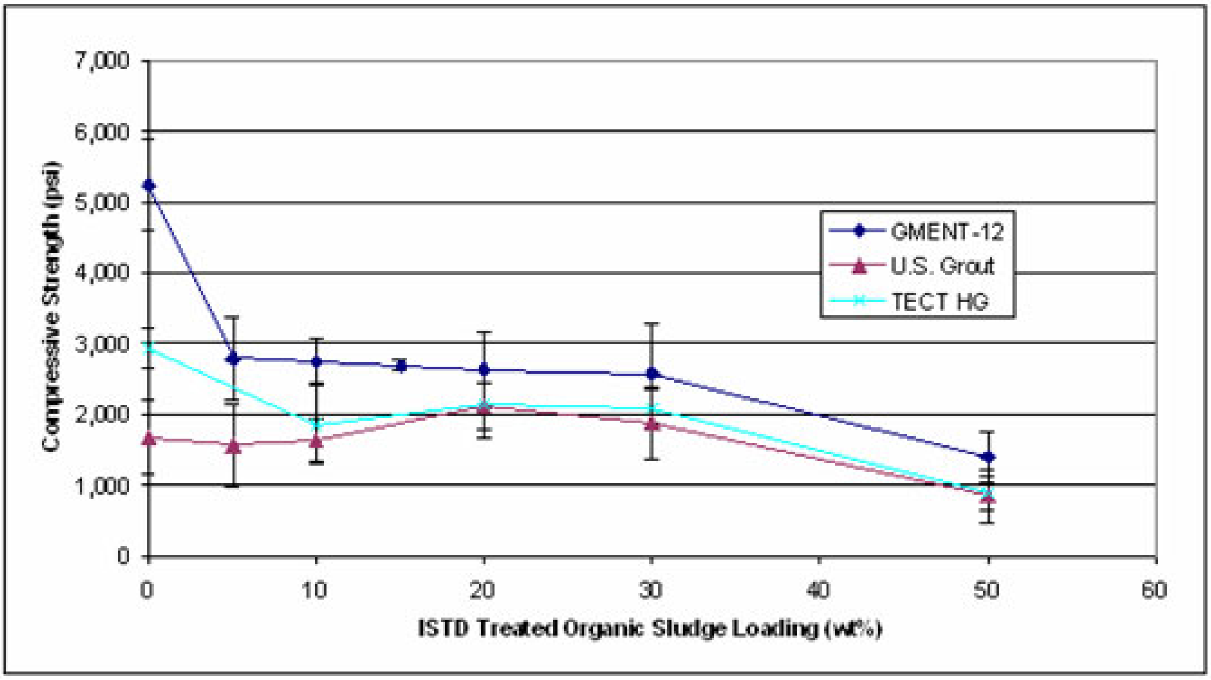

Figure 16. Compressive strength of cementitious grouts for neat grout and thermally desorbed waste loadings (Soo and Milian 2001).

The compressive strength values for all thermal desorption treated sludge waste loadings were above the minimum 60 psi required by the NRC (NRC 1991) to provide adequate support to the overlying material.

4.3.1.3 Portland-Cement-Based Grouts (Including Sodium Sulfide) and Acid Pit Soil Tests. Test specimens were prepared using soil from the SDA's Acid Pit spiked with mercury and mixed with two forms of several types of grout (Milian et al. 1997). Grouts tested include: TECT HG, TECT, Portland Type I Cement, and Portland Type H Cement. The initial use of these specimens was for compressive strength testing. After the compressive strength tests were completed, the size of the specimens was reduced to meet requirements for toxicity characteristic leaching procedure (TCLP) tests.

Grout compositions and grout and soil mixture formulations for compressive strength and leach test specimens are shown in Table 19. Sodium sulfide was added to half of the grout (except TECT HG) to investigate its capability to stabilize mercury during leaching tests. The amount of sodium sulfide mixed with the grout was set at 2 wt% of the soil mass. Contaminants in the Acid Pit soil included metals, radionuclides, organics, and nonmetal inorganics. The initial soil samples contained some mercury, but it was less than the average for Acid Pit soil. Therefore, additional mercury was added to the soil samples to reach an average concentration of 927 ppm.

Table 19. Grout compositions and test specimen formulations for grout and Acid Pit soil.

Grout Type	Weight of Solid	Weight of Liquid	Density of Grout	Specimen Grout (wt%)	Specimen Soil (wt%)
TECT/TECT HG	200 g powder	72.4 g liquid	2.27 g/cm^3	71	29
Portland Type I	50 g powder	50 g liquid	1.49 g/cm^3	57	43
Portland Type H	50 g powder	50 g liquid	1.49 g/cm^3	57	43

Cylindrical test specimens 1.5 in. in diameter and 3 in. long were cast, cured, and compression tested using ASTM C39 (2003). Table 20 presents the results of these compression tests. The TECT HG compressive strength values are somewhat lower than the Idaho Cleanup Project results discussed in Section 4.2.1.2.1. The compressive strength of TECT HG and Portland Type I cement are equivalent and are about a factor of three higher than the Portland Cement Type H values.

Table 20. Compressive strength results from grout-soil and grout with an additive/soil.

Grout Type	Average Compressive Strength (psi)	Standard Deviation (psi)
TECT HG[a]	1,880	543
TECT I[a]	2,210	262
Portland Type I Cement[b]	1,600	68
Portland Type H Cement[b]	610	65
TECT 1 with Sodium Sulfide[c]	1,900	382
Portland Type I Cement with Sodium Sulfide[d]	1,050	72
Portland Type H Cement with Sodium Sulfide[d]	640	43

a. 71 wt% grout, 29 wt% soil
b. 57 wt% grout, 43 wt% soil
c. 71 wt% grout, 29 wt% soil, sodium sulfide at 2 wt% of the soil mixed in grout liquid
d. 57 wt% grout, 43 wt% soil, sodium sulfide at 2 wt% of the soil mixed in grout liquid.

Results from Table 22 indicate that compressive strength for TECT and Portland Type H grouts are not appreciably affected by the addition of sodium sulfide to the grout. Portland Type I cement grout experiences about a 34% decrease in compressive strength, but the minimum value remains relatively high. Compressive strength values for all cementitious grouts with Acid Pit soil sample waste loadings are above the minimum of 60 psi required by the NRC (NRC 1991). This leaves open an option to use any of these grout formulations with sodium sulfide mixtures if the results from the TCLP leach tests show that mercury leaching must be reduced.

4.3.1.4 TECT Grout with Soil and Simulated Organic Waste Tests. Specimens comprised of mixtures of TECT grout, simulated waste, and soil were tested for compressive strength (Milian et al. 1997). Before selecting mixture ratios for simulated waste and TECT, the following were studied: compatibility and formulation of the individual components of the simulated waste, canola oil, sodium nitrate, and soil. TECT had only a small miscibility with the canola oil. When oil was mixed with soil, as the oils would be expected to be mixed with sorbant materials or soil in the SDA, miscibility problems between oil and grout were overcome. Mixing sodium sulfate (at ratios ranging from 5 to 67 wt%) with TECT grout resulted in a 6 to 7°C (42.8 to 44.6°F) temperature drop and quick setting after stirring was discontinued. Final setting to a hard, brittle compound was delayed, although full solidification was achieved after 30 days.

Optimized mixtures of TECT grout and soil were also tested. With soil or waste loadings of 67 wt%, the grout and soil mixture was very dry and clumpy. Addition of up to 4.8 wt% water did not significantly improve the mixture fluidity. As a result, the soil and waste loadings were reduced. Table 21 summarizes the formulation for the grout, soil, and waste mixtures. The mixture ratio for soil represents a grout-to-soil volume ratio of about 1:1.

Table 21. TECT grout waste form formulation and unconfined compressive strength results.

		Percent Waste (wt%)				
Waste Form Type	Percent TECT (wt%)	Canola Oil	Sodium Nitrate	Soil from Idaho National Laboratory Site	Average Compressive Strength (psi)	Standard Deviation (psi)
TECT/Waste	60	4	8	28	1,424	296
TECT/Soil from Idaho National Laboratory Site	57	0	0	43	2,966	413

Unconfined compressive strength results are also included in Table 23. These tests were conducted in accordance with ASTM D39. Five replicates were performed for both the TECT-soil and the TECT-simulated waste. Results show that all measured compressive strength values were above the minimum 60 psi required by the NRC (NRC 1991) to provide adequate support to the overlying material.

4.3.2 Fracture Formation

Substantial cracks in the grouting may allow water to penetrate to locations where contaminants may be mobilized and transported. Changes in concrete volume can result in crack formation if the concrete is restrained. Generally, concrete volume changes occur as a result of expansion or contraction caused by changes in temperature or moisture. Chemical effects, such as carbonation shrinkage or sulfate attack, can also result in volume changes.

Cracking of the cementitious grouts in the SDA should not be extensive. The grout in the SDA generally should not be highly restrained and shrinkage as the grout sets and dries should not result in excessive stresses. Results from earlier INL Site-sponsored grout testing (summarized in Loomis et al. 2002) showed the grouted monoliths were free of voids; extensive cracking was not obvious from the photographs. As shown in Section 4.2.1, the temperatures in the SDA remain at relatively constant levels over time and significant stresses should not result from temperature changes. The discussion in Section 4.2.3 indicates that the moisture content of the soil in the SDA is also relatively constant throughout the year, which should preclude large swings in volume caused by drying or wetting of the grout.

4.4 Contaminant Migration Indicators with Subsurface Disposal Area Interferences

Contaminant migration depends on a range of factors, including the form of the contaminant (i.e., physical or chemical), the type of grout mixed with the waste, and environmental conditions of the site. Migration is not measured directly; the long-term value is estimated based on multiple short-term tests, including hydraulic conductivity, porosity, and leaching. Section 4.4 presents the results of tests performed with selected grouts and SDA waste and waste surrogates.

4.4.1 Permeability with Subsurface Disposal Area Interferences

An important performance characteristic for grout as an immobilization agent is the rate at which water will penetrate the grout-waste mixture. Both hydraulic conductivity and porosity provide a measure of the capability of water and soluble waste materials to permeate grout. Hydraulic conductivity is an indicator of the ability of the grout to encapsulate the mixture of soil and waste and prevent percolated water from moving through this mixture. Small hydraulic conductivity values indicate a high resistance to the penetration of water, a highly desirable characteristic for restricting transport of soluble waste material. Porosity gauges the available pore space that will support diffusion of water and waste. Small values of porosity are desired to limit waste transport.

4.4.1.1 Hydraulic Conductivity. Results of hydraulic conductivity tests from several different sources are available to examine the effects of waste types and waste loading on cementitious grouts. The following subsections provide a brief summary of these results.

4.4.1.1.1 Results of Idaho National Laboratory Site Hydraulic Conductivity Tests—Portland-cement-based grout was tested for hydraulic conductivity of soil and waste loadings covering the range of conditions expected in the SDA. Grout hydraulic conductivity test results are presented for:

- No waste loading (i.e., neat grout)
- Grout and soil mixtures
- Grout and simulated organic sludge mixtures
- Grout and nitrate salt mixtures
- Grout and mixtures of thermally desorbed organic sludge.

The objective of these tests was to establish a base hydraulic conductivity with no waste loading for cementitious grouts, and then determine whether a range of waste loadings adversely affect hydraulic conductivity.

Initial hydraulic conductivity tests (Loomis et al. 2002) were performed following the essential steps of ASTM D5084 (ASTM 1990). The hydraulic conductivity results are accurate to about 10^{-8} cm/sec, based on the accuracy of measurements taken during the test. Two replicate tests were performed for the neat grout and for each grout and waste mixture with the exception of Saltstone, for which only one neat grout measurement was taken. Table 22 provides results from these tests and Figure 17 shows the trends in the hydraulic conductivity data.

Hydraulic conductivity also was tested on cementitious grouts containing 30 wt% ash that remained following in situ thermal desorption (ISTD) for organic waste (Yancey 2005). These tests used the falling head method according to ASTM D5084 (ASTM 1990). Head measurements were taken over 12 days. The hydraulic conductivity results are accurate to about 10^{-8} cm/sec, based on the accuracy of measurements taken during the test. Three replicates of the grouts and ISTD waste mixtures were tested. Saltstone was not included in this ISTD ash hydraulic conductivity testing.

4.4.1.1.2 TECT Grout with Soil and Simulated Waste Tests—The hydraulic conductivity of TECT grout with soil from the INL Site and with simulated waste (Milian et al. 1997) was measured using the constant head method according to ASTM Method D5084 (ASTM 1990). A pressure differential across the test specimen of 210 kPa (30 psi) was established from the end containing water to the end that was initially dry. The pressure difference was maintained for about 24 hours and the inflow and outflow of water was measured.

Table 22. Hydraulic conductivity for combinations of cementitious grouts and different types of waste.

	Hydraulic Conductivity							
	GMENT-12		TECT HG		U.S. Grout		Saltstone	
Waste Type	Average (cm/sec)	95% CI[a] (cm/sec)	Average (cm/sec)	95% CI[a] (cm/sec)	Average (cm/sec)	95% CI[a] (cm/sec)	Average (cm/sec)	95% CI[a] (cm/sec)
Neat Grout[b]	7.30 E-9	4.22 E-9	5.75 E-9	4.18 E-9	1.80 E-8	1.03 E-9	1.20 E-8	N/ID[d]
50% INL Soil[b]	8.00 E-9	2.06 E-9	1.40 E-8	6.19 E-9	1.15 E-8	8.77 E-9	8.00 E-8	0.0
9% Organic Sludge[b]	3.00 E-9	1.03 E-9	3.00 E-9	2.06 E-9	1.50 E-8	5.16 E-9	3.00 E-8	1.03 E-8
12% Nitrate Sludge[b]	2.85 E-7	2.22 E-7	1.30 E-8	7.22 E-9	1.35 E-8	6.70 E-9	2.00 E-8	0.0
ISTD Sludge[c]	1.40 E-8	2.9 E-10	1.38 E-8	2.54 E-9	1.13 E-8	1.15 E-9	N/ID[d]	N/ID[d]

a. 95% confidence interval.
b. Loomis et al. (2002).
c. Yancey et al. (2005).
d. No data or insufficient data.

INL = Idaho National Laboratory
ISTD = in situ thermal desorption

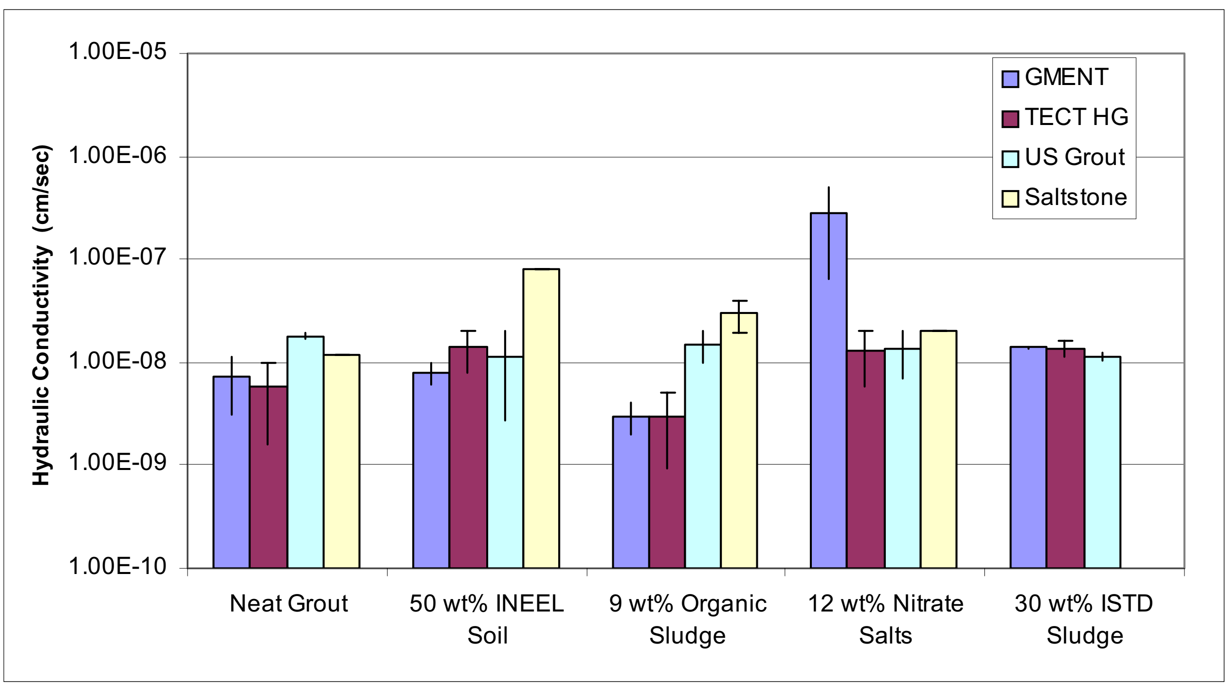

Figure 17. Hydraulic conductivity of neat grout and grout mixed with soil and waste.

The TECT grout/simulated waste composition was 60 wt% TECT, 4 wt% canola oil, 8 wt% sodium nitrate, and 28 wt% soil from the INL Site. The TECT grout/soil from the INL Site waste form composition was 57 wt% TECT grout and 43 wt% soil from the INL Site. The hydraulic conductivity measurement limits for the tests with TECT grout and the waste and soil mixtures were 2.0×10^{-11} cm/sec. Results from the tests indicated the hydraulic conductivity was less than the measurement limit. Consequently, hydraulic conductivity was reported as less than 2.0×10^{-11} cm/sec for both waste types. Each waste type was tested only once because of the proximity of the results to the lower measurement limit.

The hydraulic conductivity value reported by Milian et al. (1997) for TECT grout is over three orders of magnitude less than the Portland-cement-based grout they tested. This value is also two to three orders of magnitude less than the INL Site results. The higher values from the INL Site tests are attributed to differences in the reported measurement accuracy (10^{-11} for tests from Milian et al. versus 10^{-8} for the INL Site tests) and possibly to differences in the method of measuring hydraulic conductivity (the constant head method versus the falling head method). Results of both Milian and INL Site hydraulic conductivity tests are substantially less than the hydraulic conductivity of SDA soil, which is reported to range from 6.94×10^{-4} to 1.1×10^{-8} cm/s, with an arithmetic mean hydraulic conductivity of 1.52×10^{-4} cm/s (McCarthy and McElroy 1995).

4.4.1.2 Porosity. Diffusion of liquids or gases through grout is controlled by pathways formed by interconnected pores. Porosity is an important parameter in modeling the rate of contaminant release from a grout and was measured during INL Site testing (Yancey et al. 2005).

Porosity is defined as the ratio of the volume of void spaces to the total volume of the sample. Measurement of the volume of the void spaces was accomplished by saturating grout samples with water. Initially the samples were flushed with carbon dioxide to eliminate air from all pores that are interconnected with the outside of the sample. The samples were then saturated with de-aerated water under a vacuum. Water used in the test was made to simulate groundwater at the SDA. ASTM standards for saturating samples to determine hydraulic conductivity (ASTM 1990) and methods described in other pertinent literature (Dane and Topp 2002) were used in performing the measurements.

GMENT, TECT HG, and U.S. Grout were tested in the form of a neat grout and with a 50% soil loading. Table 23 provides results from the porosity tests and Figure 18 shows the plotted data. The GMENT and TECT HG neat grout porosities were very similar, about 37% voids, while the neat U.S. Grout had greater than 50% voids. Addition of 50% soil did not change the porosity substantially, even though the soil is estimated to have about 45 to 50% voids. Figure 18 has a line representing this estimated porosity value for the soil alone. These results indicate that porosity of the waste matrix is generally reduced by the addition of the grouts.

Table 23. Porosity for neat grout and 50% soil from Idaho National Laboratory Site.

	Porosity (Void Volume/Total Volume)					
	GMENT-12		TECT HG		U.S. Grout	
Waste Type	Average	95% CI[a]	Average	95% CI[a]	Average	95% CI[a]
Neat Grout	0.3772	0.0512	0.3773	0.0185	0.5424	0.0383
50% soil from Idaho National Laboratory Site	0.3890	0.0148	0.3511	0.0440	0.4741	0.0194

a. 95% confidence interval.

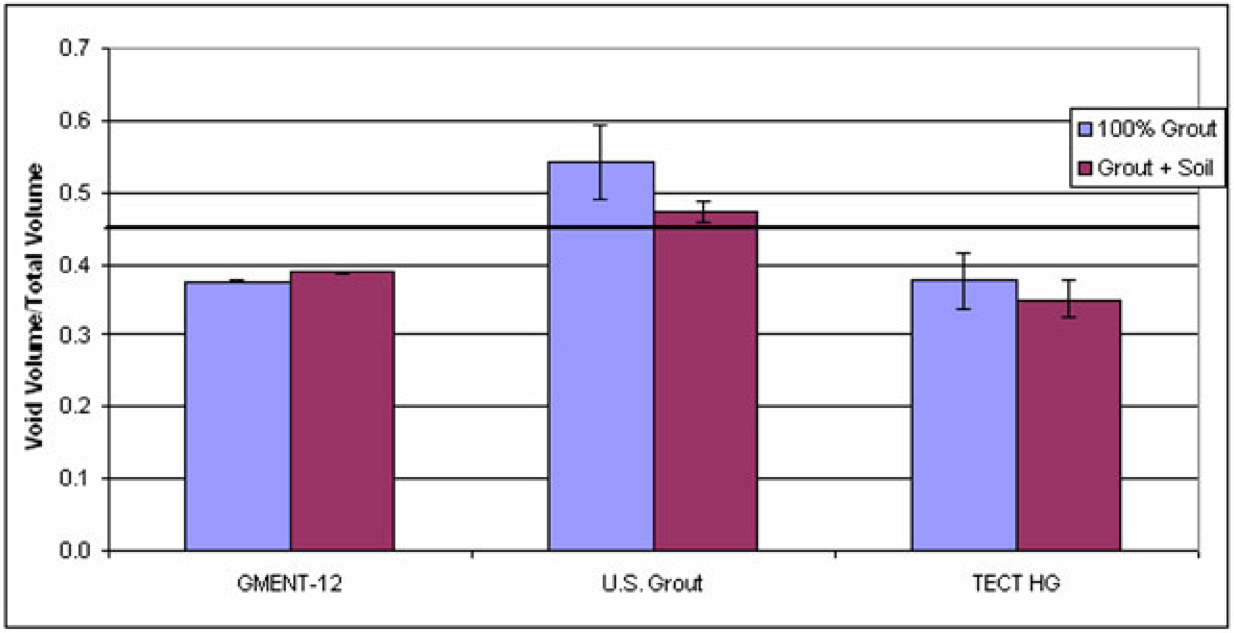

Figure 18. Porosity of neat grout and grout mixed with 50% soil from Idaho National Laboratory Site. Solid line indicates average porosity of Subsurface Disposal Area soil (Soo and Milian 2001).

4.4.2 Leachability for Subsurface Disposal Area Conditions

A key function of grouts is to reduce contaminant mobility by macroencapsulation of the contaminant, by chemical interaction that binds the contaminant, or by a combination of these two processes. Results from leach tests for grout-waste combinations indicate the capability of grouts to restrict the spread of contaminants over time. A high resistance to leaching (i.e., a low diffusion rate for contaminants) is desired. A brief summary of results is presented in this report; a more detailed discussion of leach test results is available in the *Pre-Remedial Design Report of Remediation Options for OU 7-13/14* (Matthern et al. 2005). The information in this summary is representative of the contaminants and of grouts that may be used in the SDA. Experimental leach results for both radioactive and nonradioactive contaminants are presented.

4.4.2.1 Idaho Cleanup Project Leach Test Results. The mobility of selected radionuclide contaminants for a range of cementitious grouts was measured during recently completed INL Site-sponsored testing (Yancey et al. 2005). All testing used the abbreviated ANS 16.1 leaching protocol. The purpose of these leach tests was to provide a basis for comparison of contaminant mobility among the various grout and waste mixtures. Although the leach tests are short term compared to the leach processes that will occur over hundreds and thousands of years, tests conducted using ANS 16.1 do provide an estimate of contaminant mobility based on the chemistry of cement that is relatively "new" (i.e., not aged).

The leach index measured during leach testing is related to the effective diffusivity of the contaminant as shown in Equation (3):

$$L = \log(1/D) \tag{3}$$

where:

L	=	leach index
D	=	effective diffusivity.

The leach index, rather than the effective diffusivity, is used to compare results because it is less sensitive to small changes in measured values. A lower leach index indicates a higher effective diffusivity and increased mobility of the contaminant under the conditions tested. ANS 16.1 specifies right cylindrical samples having dimensions of 5.1 × 10.2 cm (2 × 4 in.). For the reported tests, 1.9 × 3.1-cm (0.75 × 1.2-in.) samples were prepared to conserve valuable actinide tracers, and to decrease radiological control concerns. The calculations for leach indexes account for sample dimensions, so that the results reported here are comparable to those that would be measured for 5.1 × 10.2-cm (2 × 4-in.) samples. The test is a very short-term measurement compared to the leach processes that will occur over hundreds and thousands of years, but ANS 16.1 provides an estimate of contaminant mobility in a waste form.

Two groups of leach tests are presented: (1) tests for selected non-TRU radionuclides typical of those found in the SDA, and (2) tests for important TRU radionuclides found in the SDA. The selected radionuclides for the non-TRU experiments were I-129, C-14, and Tc-99. The TRU radionuclides used in the TRU experiments were uranium, plutonium, americium, and neptunium.

Since the non-TRU waste in the SDA is expected to consist primarily of debris in soil, the non-TRU experiments examined a single type of waste form: soil spiked with radionuclides mixed with grout. Two sets of experiments used different types of grout. The first set of non-TRU in situ grouting testing focused on the commercially-available, proprietary grout formulations: TECT HG, GMENT-12, U. S. Grout, and Saltstone. Since three of these grouts are Portland-cement-based, the performance of nonproprietary Portland-cement-based grout formulations was evaluated during a second set of non-TRU experiments to supplement the initial non-TRU in situ grouting test results. These experiments included the following grout formulations: Portland cement, Portland cement with fly ash, Portland cement with slag, Portland cement with fly ash and sodium thiosulfate, and Portland cement with slag and sodium thiosulfate. Each sample contained 50 wt% soil that was spiked with Tc-99, I-129, and C-14. The samples were done in triplicate. All three isotopes were detected in the leachate for each grout. For Tc-99, the leach index values were in the range of 7.0 to 13.6 (based on means and standard deviations), with U.S. Grout and TECT HG being at the low end of the range (below 8), and the remaining grouts being above 9.5. For I-129, the leach index values were in the range of 6.3 to 10.7 (based on means and standard deviations), with no clear difference among the grouts. For C-14, the leach index values were in the range of 6.4 to 18.6 (based on means and standard deviations), with U.S. Grout and TECT HG being at the low end of the range (below 9), and the remaining grouts being above 10.

Tests conducted for the in situ grouting of TRU contaminants evaluated three grout formulations (i.e., U.S. Grout, GMENT-12, and TECT HG) with three waste surrogates (i.e., soil, organic sludge, and inorganic sludge), and two types of waste (i.e., organic sludge and Pad A nitrate salts). The waste surrogates were spiked with four radionuclides: plutonium, uranium, americium, and neptunium. Surrogate actinide concentrations were selected based on isotope and median concentration data from Blackwood and Hoffman (2004). Concentrations of natural uranium, ^{239}Pu, ^{237}Np, and ^{241}Am were as close as possible to the medians specified, but with considerations for both instrument detection limits for leachate analysis and radiological control practices. Concentrations of radionuclides in the leachate were measured with inductively-coupled plasma – mass spectroscopy (ICP-MS). Waste surrogates were spiked with the four nuclides; the surrogate was mixed with each of the grout types at a ratio of 30 wt%.

Even though the concentrations of radionuclides in the surrogates were more than twice the concentrations in the organic waste (for most of the combinations tested of grouts, waste types, and TRU radionuclides), the concentrations of radionuclides (i.e., plutonium, uranium, americium, or neptunium) in the leachate were below the detection limit of the ICP-MS. The detection limit of the ICP-MS is different for each radionuclide; the instrument is calibrated with standards before each set of analyses to determine the detection limit. When the measured value for the radionuclide in the leachate was below the detection limit of the ICP-MS, the detection limit value for that radionuclide was used in the leach index calculations. Using the detection limit for minimum measurements values results in the calculation of minimum leach index values, which is worst case when considering contaminant mobility.

For the 30 wt% soil in grout tests, none of the radionuclide leachate measurements was above detection limits. Based on the detection limits, the minimum leach index for each of the U.S. Grout, GMENT-12, and TECT HG was greater than 11. Organic sludge surrogate was mixed with the same grouts at 5 and 9 wt% loadings. For 5 wt% organic sludge surrogate in grout, the leach index was greater than or equal to 9.4 for all samples, and, for 9 wt%, the leach index was greater than or equal to 10.0 for all samples. Inorganic sludge surrogate was mixed with grout at 30 and 60 wt% loadings. For 30 wt% inorganic sludge surrogate in grout, the leach index was greater than or equal to 11.0 for all samples, while, at 60 wt% loading, the leach index was greater than or equal to 12.3 for all samples.

Tests using waste containing TRU radionuclides produced results similar to those obtained with surrogates. For the 12 wt% samples of Pad A nitrate salt in grout (U. S. Grout, GMENT-12, and TECT HG), the leach index was greater than or equal to 7.6 for all samples. Organic sludge waste from Pit 9 was combined with grout at 5, 9, and 15 wt% loadings of sludge waste. For the 5 wt% loading samples, the leach index was greater than or equal to 10.4 for Am, Pu, and U in all grouts; for the 9 wt% loading samples, the leach index was greater than or equal to 11.0 for Am, Pu, and U in all grouts; and, for the 15 wt% loading samples, the leach index was greater than or equal to 10.8 for Am, Pu, and U in all grouts. For Np in all grouts, the minimum leach index was lower: at 5 wt% loading, the leach index was greater than or equal to 7.0; at 9 wt% loading, the leach index was greater than or equal to 6.5; and, at 15 wt% loading, the leach index was greater than or equal to 7.8.

For the INL Site-sponsored leach tests, it was expected that the leach index would decrease as the waste loading increased. This was not observed as the concentrations of radionuclides in the leachate were below the detection limit so that the leach index was calculated from the detection limit. Most of the leach indices are greater than 10, indicating a low effective diffusivity and a high resistance to leaching.

4.4.2.2 Other Leach Test Results

4.4.2.2.1 Accelerated Leach Test Results—Accelerated leach tests (Milian et al. 1997) of TECT 1 grout were conducted in accordance with the standard for leach testing (ASTM C1308-95 2001). Leaching was accelerated by testing with the leaching solutions at temperatures higher than they would be in the field (i.e., at room temperature, which is about 7°C (44.6°F) higher than expected temperatures in the lower portions of the SDA).

Accelerated leach test specimens were prepared with contaminant-spiked soil. Lead(II) nitrate and chromium(III) nitrate were added to distilled water and blended with soil from the INL Site. After drying and grinding, this spiked soil was used in the simulated waste. TECT 1 grout samples were prepared with 60 wt% grout and 40 wt% spiked soil. Based on calculations, sufficient lead and chromium were added to the soil to produce a final concentration of 1,000 ppm for each of these metals in the simulated waste.

A pretest determined that a representative TECT 1 and simulated grout specimen using 300 mL of leachate was appropriate for the tests. Thirteen leachate changes were made over an 11-day period, two the first day and then one each day for the remainder of the test. Approximately 125-mL was collected for analysis at the end of each time interval. Leachates were analyzed using inductively coupled plasma spectroscopy for both lead and chromium metal concentrations. After the 11-day accelerated test, no leaching was detected for either chromium or lead (i.e., both were below the instrument detection limits: chromium less than 0.04 μg/mL; lead less than 0.14 μg/mL). These results indicate that TECT 1 grout is effective in preventing leaching of chromium and lead for the conditions tested.

4.4.2.2.2 Toxicity Characteristic Leaching Procedure—The TCLP was used for testing a mixture of several cementitious grouts (i.e., TECT HG, TECT 1, Portland Type I cement, and Portland Type H cement) and soil, and a mixture of many of these same grouts (i.e., TECT 1, Portland Type I cement, Portland Type H cement) and soil plus an additive (Heiser and Fuhrmann 1997). These tests used samples prepared from the remnants of monoliths from the compressive strength tests of Acid Pit soil. Acid Pit soil was selected for the TCLP test contaminant carrier because it was considered to be typical of soil that may be grouted at the INL Site. Mercury was chosen as the contaminant for the TCLP testing. Typical Acid Pit soil samples selected for testing were assayed and found to have relatively low mercury concentrations. To bring the mercury content of these soil samples up to a level known to exist in some soil from the INL Site, mercury chloride was added to distilled water, which was then mixed with the soil. After mixing and air-drying to remove the excess water initially mixed with the mercury chloride, the average mercury concentration was 927 ppm, based on three small samples with measured concentrations of 878 ppm, 1,004 ppm, and 898 ppm.

To examine methods for minimizing mercury leaching from the soil, additional tests were conducted on grout mixed with an additive that would retard mercury migration. Nine potential additives were initially tested for their capability to retain mercury. Three were selected for additional testing and TCLP leach tests were performed on small soil samples with 1 wt% of each of the selected additives. Sodium sulfide proved most effective in retaining mercury and was selected as the additive for the grout.

The specimens for TCLP testing were taken from the remains of the monoliths prepared for the compressive strength tests of Acid Pit soil. Table 24 shows the composition of the grouts used and the proportions of the grout and the soil/stimulant mixture. For half the samples prepared, 2 wt% (based on the soil weight) of sodium sulfide was mixed with the grouts.

Table 24. Toxicity characteristic leaching procedure grout and grout and soil/stimulant formulations.

Grout Type	Weight of Grout Powder (g)	Weight of Liquid (g)	Volume Produced (ml)	Density of Grout (g/cm^3)	Grout in Mixture (wt%)	Soil/ Simulant in Mixture (wt%)
TECT HG, TECT 1	200	72.4	120	2.27	29	71
Portland Type I	50	50	67	1.49	57	43
Portland Type H	50	50	67	1.49	57	43

The size of the test specimens used in the compressive strength tests was reduced so that all pieces were smaller than the required 1 cm (0.4 in.) at their narrowest dimension. A series of sieves were used to size the particles for the required 100 g TCLP testing sample. All particles were less than 9.5 cm (3.7 in.) and greater than 4.5 cm (1.78 in.). The procedures used for TCLP analyses for mercury were EPA SW846 Method 1311 for TCLP Extraction and EPA SW846 Method 7470, Mercury (Hg in Liquid Waste-Manual Cold Vapor Method).

The TCLP leach test results (Table 25) show that one of the two TECT HG samples was below the current limits for mercury, but the concentration of mercury in the leachate for the remaining grout samples (those without an additive) were significantly higher than the current mercury TCLP limits. For all grout samples plus a sodium sulfide mixture, the concentration of leached mercury was about half the current TCLP limit of 25 ppb. For a mixture of grout, soil, and contaminants, these results indicate that the grouts alone (with the possible exception of TECT HG) are not effective in preventing leaching of mercury. Adding a material with a high affinity for mercury, such as sodium sulfide, to the grout is effective in reducing the amount of mercury leached to levels that are below the TCLP limit.

Table 25. Toxicity characteristic leaching procedure leachate concentrations for neat grouts and grouts with a mercury-retaining additive.

Sample	Grout	TCLP Hg Limit (ppb)	Leachate Hg Concentration (ppb)
2-1	TECT HG	25	48
1-2	TECT HG	25	5.4
4-1	TECT I	25	200
4.2	TECT I	25	150
3-1	Portland-Type-I Cement	25	570
3-2	Portland-Type-I Cement	25	630
10-1	Portland-Type-H Cement	25	428
10-2	Portland-Type-H Cement	25	272
7-1	TECT I + sodium sulfide	25	0.6
7-2	TECT I + sodium sulfide	25	0.7
8-1	Portland Type I Cement + sodium sulfide	25	0.3
8-2	Portland Type I Cement + sodium sulfide	25	0.3
9-1	Portland Type H Cement + sodium sulfide	25	0.5
9-2	Portland Type H Cement + sodium sulfide	25	0.3

TCLP = toxicity characteristic leaching procedure

5. SUMMARY AND CONCLUSIONS

An extensive literature search, previous tests of in situ grouting at the INL Site, and information available from tests currently being conducted at the INL Site provided data on Portland-cement-based grouts. The review of these data and an evaluation of the expected performance of Portland-cement-based grouts is based on current and projected grouting plans for the SDA. This evaluation includes a review of behavior developed using standard test procedures applicable to grouts (e.g., contaminant leaching and compressive strength), and the behavior of possible harsh SDA conditions that could affect the long-term stability of these grouts. Results will support the feasibility study for WAG 7, OU 7-13/14. The following conclusions are based on the findings of the literature search and test data assessment.

Chemistry of Portland Cement

- Results from much of the testing done on Portland-cement-based grouts that are most representative of expected INL Site conditions are based on experiments for cement that is aged less than three to six months. The affect on these results of concrete chemical degradation because of long-term aging (i.e., 100 to 1,000 years) is currently not well defined.

Effects of Chemical Reactions on Grouts

- Short-term reactions of Portland cement are primarily related to the hydration, or cure, of the freshly cast grout. The hydration mechanisms of cement pastes are a complex series of chemical reactions, dissolutions, precipitations, exchanges, and crystallizations, which can be disturbed in many different ways.

- Many chemical species have been demonstrated to have an effect on the cure reactions of grout. Many common anions and cations can be accelerators or retarders of Portland cement. In general, for cation accelerators, $Ca^{2+} > Ni^{2+} > Ba^{2+} > Mg^{2+} > Fe^{3+} > Cr^{3+} > Cu^{2+} > La^{3+} > NH^{4+} > K^{+} > Li^{+} > Cs^{+} > Na^{+}$, while for retarders, $Cu^{2+} > Zn^{2+} > Pb^{2+}$. For anion accelerators, $OH^{-} > Cl^{-} > Br^{-} > NO_3^{-} > SO_4^{2-} > CH_3CO_2$.

- Calcium chloride is the most widely used cement accelerator. Most inorganic electrolytes, especially soluble calcium salts, accelerate the hydration reaction. Many chemical species (organic and inorganic compounds) can retard the set of grout.

Effects of Physical or Other Interactions with Grouts

- Freeze-Thaw Cycles and Wet-Dry Cycles—Relatively constant moderate temperatures and relatively constant soil-water content in the SDA preclude physical damage to Portland-cement-based grouts from freeze-thaw cycles and from shrinkage/swelling caused by changes in the moisture of surrounding material resulting from wet-dry cycles.

- The four major metals of interest with respect to corrosion in the SDA are carbon steel, stainless steel, inconel, and beryllium. Corrosion of metal is a concern in two ways. First, the products of corrosion from metal take up more volume than the original metal, leading to localized regions of stress within the cement near the encased metal. Second, the metal may contain contaminants. As the metal corrodes, the contaminants can be released from the metal. Both mechanisms are of interest in the SDA.

- Because of the use of steel in commercial construction, a lot of information about corrosion of carbon steel, especially rebar, in concrete is available in the literature. Studies of stainless steel are also available because it is used for reinforcing some commercial construction. Inconel and beryllium are not used for reinforcing and no data could be located on their behavior in concrete.

- Chloride is a major agent of attack of carbon steel within concrete, although it is not expected to be a major factor at the SDA. Carbonation and groundwater leaching of the cement in the grouted waste is expected to occur and could reduce the alkalinity (lower the pH) of the cement leading to a more corrosion favorable environment for metals.

- Leaching of Basic Cement Constituents—Results from leach tests on GMENT-12, TECT HG, U.S. Grout, and Saltstone grouts for the basic constituents of Portland cement (i.e., calcium, silicon, and aluminum) show very low rates of leaching. Using these results to calculate the timeframe when 1% of these constituents will be leached from contiguously grouted columns indicated that "tens of thousands of years" would be required (Loomis et al. 2002).

- Radiation-Induced Degradation—Accurately assessing the effect of the dose received by grouts is difficult because the initial burial records of many radioactive packages buried in the SDA do not contain isotopic content. A conservative approach indicates that radioactive doses are sufficiently high to result in a reduction of compressive strength ranging from 15 to 60%. Reductions in compressive strength within this range would not cause most grout-waste mixtures to drop below the minimum 60 psi required by the NRC (NRC 1991) to provide adequate support to the overlying material. Examination of literature results indicate that radiation-induced hydrogen generation in Portland-cement-based grout will not result in degradation of grout performance.

- Degradation of cement-based grouts can result from in situ attack by microorganisms (i.e., MIC). The MIC of concrete is a function of the macroenvironmental conditions, the changing microenvironmental conditions, and the bioavailability of nutrients and energy.

- Microbial-caused concrete degradation rates in concrete sewer structures are as high as 4.3 to 4.7 cm/yr (1.69 to 1.85 in./yr). Sewer systems offer high sulfur and nutrient concentrations, and well mixed and oxygenated aqueous conditions. Biocorrosion rates elsewhere are generally slower, ranging from 1 to 5 mm/yr (0.04 to 0.2in./yr), but studies have reported rates as high as 1 cm/yr (0.4 in./yr). Compared to the expected composition of the groundwater in the SDA at the INL Site, the solutions used in the reported studies contain more nitrogen (ammonia), phosphorous, and potassium than the groundwater and had a much lower pH, favoring acid-producing bacteria. In addition, the studies were also conducted at higher temperatures (25°C [77 °F]) than would be expected in the subsurface (7 to 10°C [44.6 to 50°F]), and the SDA provides unsaturated rather than saturated conditions. In situ degradation at the SDA would be likely to occur, but at rates slower than those reported in the literature.

- Carbonation of cement can alter the performance of cement by reducing the pH, changing the mineralogy, and altering the physical properties of the cement. Carbonation occurs when carbon dioxide (gas phase) or bicarbonate (liquid phase) diffuse into cement and react with the existing mineralogy. While carbonation is generally a slow process, the rate depends on the concentration of carbon dioxide (or bicarbonate) and the degree of hydration of the cement. The estimate of the carbonation rate for the SDA was interpolated from the carbonation rates given in the two models based on the carbon dioxide concentration in the soil at the SDA compared to the concentrations of carbon dioxide used in the models. In 1,000 years the carbonation front in the SDA is estimated to move 73.4 mm (2.89 in.) into the cemented waste.

- Groundwater leaching can degrade performance of cement over time. The NRC has developed a model to predict migration due to groundwater leaching of a 10.5 pH front into concrete. The conditions for in situ grouting at the SDA are expected to be very similar to those used for the model. The model predicts that the 10.5 pH front will move toward the center of the concrete mass at a rate of 1 m (3.3 ft) per 1.5×10^{5} years or 6.67×10^{-3} mm/yr.

- Physical Properties—Although specific information on cementitious grouts is available for the time frame of 0 to 150 years, the effect of aging on cementitious grout properties beyond this time is not well understood.

Structural Support Properties with SDA Interferences

Results of compressive strength tests from the INL Site preremedial design testing generally indicate that compressive strength values were above the minimum of 60 psi that the NRC specifies (NRC 1991) for all of the following:

- Grouts with soil loadings of 50% or less
- Organic sludge loadings of 9% or less
- Nitrate salt sludge loadings of 25% or less (except for Saltstone)
- Thermally desorbed sludge loadings of 50% or less.

Specific compressive strength results for the different interferences indicate:

- Soil—Maximum compressive strength of the tested Portland-cement-based grouts mixed with soil ranged from a high of 36.1 MPa (5,235 psi) with a 12% soil loading to a low of 9.1 MPa (1,318 psi) with a 50% soil loading. Soil loadings of 70% resulted in significantly degraded compressive strength for all grouts.

- Organic sludge—When loaded with organic waste in the range of 3 to 50%, the cementitious grout's compressive strengths were not substantially reduced for sludge loadings of 9% or less. Compressive strength for TECT HG and Saltstone was reduced by about 20 to 30% at an organic sludge loading of 12%. Organic sludge loadings of 25 and 50% resulted in very low compressive strength for all tested grouts.

- Nitrate salt—Decreases in compressive strength of about 50% at nitrate salt loadings of 25%, or less, were measured for all grouts tested except Saltstone, which had relatively large reductions in compressive strength for all nitrate salt loadings.

- Grout mixed with thermally desorbed organic waste—Compressive strength was reduced less than 50% for sludge loadings of 30% or less.

Permeability for SDA Conditions

- Hydraulic conductivity values from preremedial design testing at INL Site for grout and grout/waste mixtures were in the range of 5×10^{-6} to 5×10^{-8} cm/sec, which is about two orders of magnitude less than the average hydraulic conductivity of the SDA soil. This difference demonstrates the relative impermeability of the grouted waste when compared to the soil. Neat grout values were generally less than grout waste mixtures, although hydraulic conductivity of both GMENT-12 and TECT HG was smallest for a 9 wt% organic sludge mixture.

  The hydraulic conductivity value reported by Milian et al. (1997) for TECT grout is over three orders of magnitude less than the Portland-cement-based grout they tested. This value is also two to three orders of magnitude less than the INL Site results. The higher values from the INL Site tests are attributed to differences in the reported measurement accuracy and possibly to differences in the method of measuring hydraulic conductivity.

- Porosity testing for three proprietary grouts mixed with soil showed that two of the grouts reduced the mixture porosity by small amounts. Porosity for these mixtures does not appear to be closely coupled with hydraulic conductivity.

Leachability for SDA Conditions

- The purpose of the leach tests at the INL Site was to provide a basis for comparison of contaminant mobility among the various grout and waste mixtures. Although the leach tests are very short term compared to the leach processes that will occur over hundreds and thousands of years, the tests conducted do provide an estimate of contaminant mobility based on the chemistry of Portland cement that is relatively "new" (i.e., not aged).

- It was expected that the leach index would decrease as the waste loading increased. This was not observed as the concentrations of radionuclides in the leachate were below the detection limit so that the leach index was calculated from the detection limit. Most of the leach indices are greater than 10, indicating a low effective diffusivity and a high resistance to leaching.

- The effective diffusivity of the TRU radionuclides in the cementitious grouts was lower than the effective diffusivity of Tc-99, C-14, and I-129 in the cementitious grouts. Cementitious grouts immobilize contaminants by a combination of chemical interaction and encapsulation. The difference seen between the two classes of radionuclides with the cementitious grouts is likely to be from a difference in the chemical interactions between radionuclides and grouts.

- In the leach tests with the actual organic sludge waste, neptunium had the highest diffusivity followed by plutonium and then by americium and uranium. (The last two were approximately the same value). In leach tests with the organic sludge surrogate, the order was different, with uranium and americium having the highest apparent diffusivity, followed by plutonium. Neptunium was not added to the surrogate for organic sludge surrogates.

- Leach tests similar to those performed with the proprietary grouts and non-TRU radionuclides were conducted for nonproprietary grouts (i.e., Portland cement, Portland cement with fly ash, Portland cement with slag, Portland cement with fly ash and sodium thiosulfate, and Portland cement with slag and sodium thiosulfate). The leach results showed there are no statistically significant differences between these Portland-cement-based grouts. Comparison of the nonproprietary and proprietary results show that care should be taken in grout selection as some grouts perform better than others.

- Accelerated leach tests show that TECT grout is effective in preventing leaching of chromium and lead. The TCLP leach tests indicate that none of the cementitious grouts alone are effective in preventing mercury leaching. Adding a material with a high affinity for mercury to the grouts (about 2 wt% of sodium sulfide) reduced mercury leaching to below current limits for all cementitious grouts tested.

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